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ROYAL SOCIETY

OF

NEW SOUTH WALES

FOR

1937-1938
(INCORPORATED 1881)

VOL. LXXI

Parts I and II

EDITED BY
THE HONORARY SECRETARIES.

THE AUTHORS OF PAPERS ARE ALONE RESPONSIBLE FOR THE STATEMENTS MADE AND THE OPINIONS EXPRESSED THEREIN.

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* Published March 17, 1938.

* Published December 2, 1938.

NOTICE.

The Royal Society of New South Wales originated in 1821 as the "Philosophical Society of Australasia"; after an interval of inactivity, it was resuscitated in 1850, under the name of the "Australian Philosophical Society", by which title it was known until 1856, when the name was changed to the "Philosophical Society of New South Wales"; in 1866, by the sanction of Her Most Gracious Majesty Queen Victoria, it assumed its present title, and was incorporated by Act of the Parliament of New South Wales in 1881.

TO AUTHORS.

Authors should submit their papers in typescript and in a condition ready for printing. All physico-chemical symbols and mathematical formulæ should be so clearly written that the compositor should find no difficulty in reading the manuscript. Sectional headings and tabular matter should not be underlined. Pen-illustrations accompanying papers should be made with black Indian ink upon smooth white Bristol board. Lettering and numbers should be such that, when the illustration or graph is reduced to 3½ inches in width, the lettering will be quite legible. On graphs and text figures any lettering may be lightly inserted in pencil. Photomicrographs should be rectangular rather than circular, to obviate too great a reduction. The size of a full page plate in the Journal is 4 × 6¼ inches, and the general reduction of illustrations to this limit should be considered by authors. When drawings, etc., are submitted in a state unsuitable for reproduction, the cost of the preparation of such drawings for the process-block maker must be borne by the author. The cost of colouring plates or maps must also be borne by the author.

FORM OF BEQUEST.

I bequeath the sum of £ to the Royal Society of New South Wales, Incorporated by Act of the Parliament of New South Wales in 1881, and I declare that the receipt of the Treasurer for the time being of the said Corporation shall be an effectual discharge for the said Bequest, which I direct to be paid within calendar months after my decease, without any reduction whatsoever, whether on account of Legacy Duty thereon or otherwise, out of such part of my estate as may be lawfully applied for that purpose.

[*Those persons who feel disposed to benefit the Royal Society of New South Wales by Legacies, are recommended to instruct their Solicitors to adopt the above Form of Bequest.*]

PUBLICATIONS.

The following publications of the Society, if in print, can be obtained at the Society's Rooms, Science House, Gloucester and Essex Streets, Sydney.

Transactions of the Philosophical Society, N.S.W., 1862–5, pp. 374, out of print.

Vols.	I–XI	Transactions of the Royal Society, N.S.W.,			1867–1877			,,
,,	XII	Journal and Proceedings	,,	,,	1878,	pp.	324,	price 10s. 6d.
,,	XIII	,, ,, ,,	,,	,,	1879,	,,	255,	,,
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Royal Society of New South Wales

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LIST OF THE MEMBERS

OF THE

Royal Society of New South Wales

P Members who have contributed papers which have been published in the Society's Journal. The numerals indicate the number of such contributions.

‡ Life Members.

Elected.		
1908		Abbott, George Henry, B.A., M.B., Ch.M., 185 Macquarie-street, Sydney; p.r. "Westchester," Fairfax-road, Bellevue Hill.
1935		Albert, Michel Francois, "Boomerang," Billyard-avenue, Elizabeth Bay.
1898		Alexander, Frank Lee, Surveyor, 21 George-street, Parramatta; p.r. 154 William-street, Granville.
1905	P 3	Anderson, Charles, M.A., D.Sc. (*Edin.*), C.M.Z.S., Director of the Australian Museum, College-street, Sydney; p.r. 17 Towns-road, Vaucluse. (Hon. Secretary.) (President, 1924.)
1909	P 11	Andrews, Ernest C., B.A., Hon. Mem. Washington Academy of Sciences and of Royal Society of New Zealand, No. 4, "Kuring-gai," 241 Old South Head-road, Bondi. (President, 1921.)
1933		Andrews, John, B.A., Ph.D., Lecturer in Geography in the University of Sydney; p.r. 20 Woolwich-road, Hunter's Hill.
1935		Ash, Percy Arthur, D.D.S., University Lecturer, 135 Macquarie-street, Sydney.
1930		Aston, Ronald Leslie, B.Sc., B.E. *Syd.*, M.Sc., Ph.D., *Cantab.*, A.M.I.E.Aust., Lecturer in Civil Engineering and Surveying in the University of Sydney; p.r. 24 Redmyre-road, Strathfield.
1919	P 1	Aurousseau, Marcel, B.Sc., 16 Woodland-street, Balgowlah.
1935		Back, Catherine Dorothy Jean, M.Sc., The Women's College, Newtown.
1878		Backhouse, His Honour Judge A. P., M.A., "Melita," Elizabeth Bay.
1924	P 1	Bailey, Victor Albert, M.A., D.Phil., F.Inst.P., Assoc.-Professor of Physics in the University of Sydney; p.r. 12 Cranbrook-avenue, Cremorne.
1919		Baker, Henry Herbert, F.S.M.C., c/o W. Watson & Son Ltd. Watson House, Bligh-street, Sydney; p.r. 18 Bradley's Head-road, Mosman.
1894	P 28	Baker, Richard Thomas, The Crescent, Cheltenham.

Elected.		
1934	P 1	Baker, Stanley Charles, M.Sc., Teacher of Physics, Technical College, Newcastle; p.r. 40 Hebburn-street, Hamilton, N.S.W.
1937		Baldick, Kenric James, Research Scholar, 19 Beaconsfield-parade, Lindfield.
1919		Bardsley, John Ralph, 76 Wright's-road, Drummoyne.
1895	P 9	Barraclough, Sir Henry, K.B.E., B.E., M.M.E., M.Inst.C.E., M.I.Mech.E., Memb. Soc. Promotion Eng. Education; Memb. Internat. Assoc. Testing Materials: Professor of Mechanical Engineering in the University of Sydney.
1935		Bayley, Arthur, 6 Martin-road, Centennial Park.
1933		Bedwell, Arthur Johnson, Eucalyptus Oil Merchant, "Kama," 10 Darling Point-road, Edgecliff.
1926		Bentivoglio, Sydney Ernest, B.Sc.Agr., c/o Tooth & Co. Limited, Sydney; p.r. 52 Crows Nest-road, Wollstonecraft.
1937	P 4	Birch, Arthur John, M.Sc., 36 Ebley-street, Waverley.
1923		Birks, George Frederick, Wholesale Druggist, c/o Potter & Birks Ltd., 15 Grosvenor-street, Sydney; p.r. 42 Powell-street, Killara.
1916		Birrell, Septimus, 74 Edinburgh-road, Marrickville.
1920		Bishop, Eldred George, Manufacturing and General Engineer, 37-45 Myrtle-street, Chippendale; p.r. 17 Thompson-street, Clifton Gardens.
1905		Blakemore, George Henry, M.I.M.M., "Wawoona," 10 Cooper-street, Strathfield.
1888		‡Blaxland, Walter, F.R.C.S. *Eng.*, L.R.C.P. *Lond.*, "Inglewood," Florida-road, Palm Beach, N.S.W.
1933		Boan, Robert Farquharson, A.A.C.I., Analyst and Consulting Chemist, 185 Elizabeth-street, Sydney.
1933	P 12	Bolliger, Adolph, Ph.D., Director of Research, Gordon Craig Urological Research Laboratory, Department of Surgery, University of Sydney.
1926	P 5	Booker, Frederick William, M.Sc., c.o. Geological Survey, Mines Department, Sydney.
1920	P 9	Booth, Edgar Harold, M.C., D.Sc., F.Inst.P., New England University College, Armidale. (President, 1935.)
1922		Bradfield, John Job Crew, C.M.G., D.Sc. *Eng.*, M.E., M.Inst.C.E., M.Inst.E.Aust., Barrack House, 16 Barrack-street, Sydney; p.r. 23 Park-avenue, Gordon.
1938		Breckenridge, Marion, B.Sc., Acting Curator, Geology Museum, University of Sydney, 28 Junction-road, Hornsby.
1919	P 1	Briggs, George Henry, B.Sc., Ph.D., F.Inst.P., Associate-Professor of Physics, University of Sydney; p.r. 13 Findlay-avenue, Roseville.
1935		Brown, Ida Alison, D.Sc., Lecturer in Palæontology, University of Sydney.
1906		Brown, James B., No. 1 Maitland-avenue, East Kew, E.4, Victoria.
1913	P 21	Browne, William Rowan, D.Sc., Assistant-Professor of Geology in the University of Sydney. (Vice-President.) (President, 1932.)

Elected.		
1898		‡Burfitt, W. Fitzmaurice, B.A., M.B., Ch.M., B.Sc. *Syd.*, F.R.A.C.S., "Wyoming," 175 Macquarie-street, Sydney; p.r. "Radstoke," Elizabeth Bay.
1926		Burkitt, Arthur Neville St. George, M.B., B.Sc., Professor of Anatomy in the University of Sydney.
1919	P 19	Burrows, George Joseph, B.Sc., Lecturer and Demonstrator in Chemistry in the University of Sydney.
1934		Carruthers, H. L., M.B., B.S., 4 Elcho-street, Hamilton, N.S.W.
1903	P 3	Carslaw, Horatio Scott, Sc.D., LL.D., F.R.S.E., Emeritus Professor of Mathematics, University of Sydney, Fellow of Emmanuel College, Cambridge; Burradoo, N.S.W.
1913	P 4	Challinor, Richard Westman, F.I.C., A.A.C.I., A.S.T.C., F.C.S., Lecturer in Organic Chemistry, Sydney Technical College; p.r. 54 Drumalbyn-road, Bellevue Hill. (Vice-President.) (President, 1933.)
1933		Chalmers, Robert Oliver, A.S.T.C., Assistant (Professional) in Mineralogy, Australian Museum, College-street, Sydney.
1913	P 19	Cheel, Edwin, 40 Queen-street, Ashfield. (Vice-President.) (President, 1931.)
1935	P 2	Churchward, John Gordon, B.Sc.Agr., Ph.D., 1 Hunter-street, Woolwich.
1935		Clark, Reginald Marcus, Central Square, Sydney.
1938		Clune, Francis Patrick, Author and Accountant, 15 Prince's Avenue, Vaucluse.
1920		Cooke, Frederick, c/o Meggitt's Limited, Asbestos House, York and Barrack-streets, Sydney.
1913	P 5	Coombs, F. A., F.C.S., Instructor of Leather Dressing and Tanning, Sydney Technical College; p.r. Bannerman-crescent, Rosebery.
1928		Coppleson, Victor Marcus, M.B., Ch.M., F.R.C.S., F.R.A.C.S., Surgeon, 225 Macquarie-street, Sydney; p.r. "Cravenna," 8 Macleay-street, Potts Point.
1933		Corbett, Robert Lorimer, Managing Director of Robert Corbett & Co. Ltd., Manufacturing Chemists, Head Office, 379 Kent-street, Sydney.
1882		Cornwell, Samuel, J.P., "Canberra," Tyagarah, N.S.W.
1919		Cotton, Frank Stanley, D.Sc., Chief Lecturer and Demonstrator in Physiology in the University of Sydney.
1909	P 7	Cotton, Leo Arthur, M.A., D.Sc., Professor of Geology in the University of Sydney. (President, 1929.)
1921	P 1	‡Cresswick, John Arthur, A.A.C.I., F.C.S., Production Superintendent and Chief Chemist, c/o The Metropolitan Meat Industry Commissioner, State Abattoir and Meat Works, Homebush Bay; p.r. 101 Villiers-street, Rockdale.
1935	P 2	Culey, Alma Gertrude, M.Sc., 37 Neirbo-avenue, Hurstville.
1912		Curtis, Louis Albert, L.S., F.I.S., V.D., Major, Surveyor, 66 Pitt-street, Sydney; p.r. 59 Albyn-road, Strathfield.

Elected.		
1890		Dare, Henry Harvey, M.E., M.Inst.C.E., M.I.E.Aust., 14 Victoria-street, Roseville.
1919	P 2	de Beuzeville, Wilfrid Alex. Watt, J.P., "Mélamere," Welham-street, Beecroft.
1894		Dick, James Adam, C.M.G., B.A. *Syd.*, M.D., C.M. *Edin.*, F.R.C.S. *Edin.*, Col. A.A.M.C., Comr. Ord. St. John, Medical Practitioner, "Catfoss," 59 Belmore-road, Randwick.
1906		‡Dixson, William, "Merridong," Gordon-road, Killara.
1913	P 3	Doherty, William M., F.I.C., F.A.C.I., 48 Malton-road, Beecroft.
1928		Donegan, Henry Arthur James, A.S.T.C., A.A.C.I., Analyst, Department of Mines, Sydney; p.r. 18 Hillview-street, Sans Souci.
1937	P 2	Dulhunty, John Allan, B.Sc., 250 Glebe-road, Glebe Point.
1924		Dupain, George Zephirin, A.A.C.I., F.C.S., Director Dupain Institute of Physical Education and Medical Gymnastics, Manning Building, 449 Pitt-street, Sydney; p.r. "Rose Bank," 158 Parramatta-road, Ashfield.
1924		Durham, Joseph, 9 Ada-street, Randwick.
1934	P 7	Dwyer, Francis P. J., M.Sc., Lecturer in Chemistry, Technical College, Sydney.

1923	P 17	Earl, John Campbell, D.Sc., Ph.D., Professor of Organic Chemistry in the University of Sydney.
1924		Eastaugh, Frederick Alldis, A.R.S.M., F.I.C., Professor in Engineering Technology and Metallurgy in the University of Sydney.
1934	P 1	Elkin, Adolphus Peter, M.A., Ph.D., Professor of Anthropology in the University of Sydney. (Hon. Secretary.)
1935		Ellis, Leon Macintosh, B.Sc.F. *Toronto*, 122 Spencer-street, Melbourne.
1935		England, Sidney Willis, 29 Queen-street, Mosman.
1937		English, James Roland, Surveyor, Water Conservation and Irrigation Commission Survey Camp, Wee Waa, N.S.W.
1916	P 2	Enright, Walter John, B.A., Solicitor, High-street, West Maitland; p.r. Regent-street, West Maitland.
1908		Esdaile, Edward William, 42 Hunter-street, Sydney.
1935		Evans, Silvanus Gladstone, A.I.A.A. *Lond.*, A.R.A.I.A., 6 Major-street, Coogee.

1921		Farnsworth, Henry Gordon, Government Stores, Harrington-street, Sydney; p.r. "Rothsay," 90 Alt-street, Ashfield.
1910		Farrell, John, A.S.T.C., Riverina Flats, 265 Palmer-street, Sydney.
1909	P 7	Fawsitt, Charles Edward, D.Sc., Ph.D., Professor of Chemistry in the University of Sydney. (President, 1919.)

Elected.		
1923		Fiaschi, Piero, O.B.E., V.D., M.D. *Columbia Univ.*, D.D.S. *New York*, M.R.C.S. *Eng.*, L.R.C.P. *Lond.*, 178 Phillip-street, Sydney.
1927	P 7	Finnemore, Horace, B.Sc., F.I.C., Lecturer in Pharmacy in the University of Sydney.
1935		Firth, Francis Williamson, Elliotts and Australian Drug Ltd., O'Connell-street, Sydney.
1935		Firth, John Clifford, B.Sc., "Avoca," Huntley's Point-road, Gladesville.
1920		Fisk, Sir Ernest Thomas, K.B., F.Inst.R.E., A.M.I.E. (*Aust.*), Chairman of Directors, Amalgamated Wireless (Australasia) Ltd., Wireless House, 47 York-street, Sydney; p.r. 16 Beaconsfield-parade, Lindfield.
1933		Fletcher, Harold Oswald, Assistant Palæontologist, Australian Museum, College-street, Sydney.
1879		‡Foreman, Joseph, M.R.C.S. *Eng.*, L.R.C.P. *Edin.*, "The Astor," Macquarie-street, Sydney.
1932		Forman, Kenn. P., M.I.Refr.E., c.o. Westinghouse Sales & Rosebery, Dunning-avenue, Waterloo.; p.r. "Wyreema," Alison-road, Randwick.
1905		Foy, Mark, c/o Geo. O. Bennett, 133 Pitt-street, Sydney.
1935		Fraser, Lilian Ross, M.Sc., 25 Bellamy-street, Pennant Hills.
1935	P 2	Garretty, Michael Duhan, M.Sc., Mining Geologist, 352 Chloride-street, Broken Hill, N.S.W.
1926		Gibson, Alexander James, M.E., M.Inst.C.E., M.I.E.Aust., Consulting Engineer, 906 Culwulla Chambers, 67 Castlereagh-street, Sydney; p.r. "Wirruna," Belmore-avenue, Wollstonecraft.
1935		Goddard, Roy Hamilton, F.C.A. *Aust.*, Royal Exchange, Bridge-street, Sydney.
1921		Godfrey, Gordon Hay, M.A., B.Sc., Lecturer in Physics in the Technical College, Sydney.
1936		Goulston, Edna Maude, B.Sc., Demonstrator in Micro-Chemistry in the University of Sydney; p.r. 83 Birriga-road, Bellevue Hill.
1938		Griffith, Christian Westmeath Jeffray, Library Assistant, Municipal Library, Sydney; p.r. "Gortmore," Jannali, N.S.W.
1938		Griffiths, Edward L., B.Sc., A.A.C.I., A.I.C., Chief Chemist, Department of Agriculture; p.r. 151 Wollongong-road, Arncliffe.
1934		Hall, Norman Frederick Blake, M.Sc., Chemist, Council for Scientific and Industrial Research (Tobacco Section), Dept. of Organic Chemistry, University of Sydney; p.r. 4 Whatmore-street, North Sydney.
1880	P 6	‡Halligan, Gerald Harnett, L.S., F.G.S., Retired Civil Engineer and Hydrographer, "The Straths," Pacific Highway, Killara.
1892		Halloran, Henry Ferdinand, L.S., 153 Elizabeth-street, Sydney.
1919		Hambridge, Frank, Adelaide Steamship Co. Chambers, 22 Bridge-street, Sydney; p.r. "The Chalet," Lucinda-avenue, Wahroonga.

Elected.			
1933			Hancock, Francis Charles, B.Sc. (Hons.), Dip.Ed. (*University of Bristol*), Fort Street Boys' High School, Petersham.
1905	P	6	Harker, George, D.Sc., F.A.C.I., Cancer Research Department, University of Sydney ; p.r. 75 Prospect-road, Summer Hill.
1936			Harper, Arthur Frederick Alan, M.Sc., A.Inst.P., Cancer Research Department, University of Sydney ; p.r. " Koonna," Rosedale-avenue, Manly.
1937	P	1	Harradence, Rita Harriet, M.Sc., Research Scholar, 27 Henley-road, Homebush West.
1934			Harrington, Herbert Richard, Teacher of Physics and Electrical Engineering, Technical College, Harris-street, Ultimo.
1923	P	3	Harrison, Travis Henry John, D.Sc.Agr., D.I.C. (*London*), Commonwealth Fruit Officer, Australia House, Strand, London, England ; p.r. 41 Queen's Gardens, Ealing, W.5, London.
1929			Hawley, J. William, J.P., Financial Agent, 4 Castlereagh-street, Sydney ; p.r. 12 King's-road, Vaucluse.
1934			Hayes, William Lyall, A.S.T.C., A.A.C.I., Works Chemist, c/o Messrs. Wm. Cooper & Nephews (Aust.) Ltd., Phillip-street, Concord ; p.r. 30 Cormiston-avenue, Central Concord.
1919			Henriques, Frederick Lester, 208 Clarence-street, Sydney.
1935			Hewitt, Frank Rupert, 7 Tindale-road, Artarmon.
1938			Hill, Dorothy, M.Sc. (*Q'ld.*), Ph.D. (*Cantab.*), Geological Research Fellow, University of Queensland, Brisbane.
1918			Hindmarsh, Percival, M.A., B.Sc.Agr., Principal, Agricultural High School, Yanco.
1936			Hirst, Edward Eugene, General Manager, British General Electric Co. Ltd. ; p.r. " Springmead," Ingleburn.
1928			Hirst, George Walter Cansdell, B.Sc., A.S.T.C. (Sc.), A.M.I.E. (*Aust.*), A.M.Inst.T., c/o Chief Mechanical Engineer's Office, N.S.W. Railways, Wilson-street, Redfern ; p.r. " St. Cloud," Beaconsfield-road, Chatswood.
1916			Hoggan, Henry James, A.M.I.M.E. (*Lond.*), A.M.I.E. (*Aust.*), Consulting and Designing Engineer, " Lincluden," 81 Frederick-street, Rockdale.
1930			Holmes, James Macdonald, Ph.D., F.R.G.S., F.R.S.G.S., Associate Professor of Geography in the University of Sydney.
1919			Hoskins, Arthur Sidney, Engineer, Steel Works, Port Kembla ; postal address, P.O. Box 36, Wollongong.
1919			Hoskins, Cecil Harold, Engineer, c/o Australian Iron & Steel Ltd., Kembla Building, 58 Margaret-street, Sydney, Box 3375 R, G.P.O.
1935			Howarth, Mark, Grange Mount, Bull-street, Mayfield, Newcastle, N.S.W.
1936			Howie, Sir Archibald, K.B., M.L.C., 7 Wynyard-street, Sydney.
1938			Hughes, Gordon Kingsley, University Lecturer, University of Sydney.

Elected.		
1923	P 3	‡Hynes, Harold John, D.Sc., B.Sc.Agr., Senior Asst. Biologist, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. "Belbooree," 10 Wandella-avenue, Roseville.
1935		James, Hugh, A.C.I.S., 55 Macquarie-street, Sydney.
1929		Jeffrey, Robert Ewen, A.A.C.I., Managing Director, Bardsley's Ltd.; p.r. 9 Greycliffe-avenue, Vaucluse.
1909	P 15	Johnston, Thomas Harvey, M.A., D.Sc., C.M.Z.S., Professor of Zoology in the University of Adelaide. (Cor. Mem., 1912.)
1924		Jones, Leo Joseph, Government Geologist, Department of Mines, Sydney.
1935	P 4	Joplin, Germaine Anne, B.Sc., Ph.D., Curator of the Geological Department Museum, University of Sydney; p.r. 18 Wentworth-street, Eastwood.
1930		Judd, William Percy, 123 Wollongong-road, Arncliffe.
1911		Julius, Sir George A., Kt., B.Sc., B.E., M.I.Mech.E., M.I.E.Aust., Culwulla Chambers, Castlereagh-street, Sydney.
1932		Keeble, Arthur Thomas, B.Sc., Science Master, Sydney Grammar School; p.r. 55 Carlotta-street, Greenwich.
1935		Kelly, Caroline Tennant (Mrs.), "The Old Parsonage," Castle Hill, N.S.W.
1935		Kelly, Francis Angelo Timothy, "The Old Parsonage," Castle Hill, N.S.W.
1934		Kelly, Francis de Vere, Pharmacist, The Sydney Drug Stores, 264 Elizabeth-street, Sydney; p.r. c/o Masonic Club, 169 Castlereagh-street, Sydney.
1924		Kenny, Edward Joseph, Geological Surveyor, Department of Mines, Sydney; p.r. 17 Alma-street, Ashfield.
1934		Kerslake, Richmond, A.S.T.C., A.A.C.I., Industrial Chemist, c/o Australian Paper Mfrs. Ltd., Macauley-street, Matraville; p.r. 55 Harold-street, Matraville.
1896		King, Sir Kelso, K.B., Underwriter, 117 Pitt-street, Sydney.
1920		Kirchner, William John, B.Sc., A.A.C.I., Manufacturing Chemist, c/o Messrs. Burroughs, Wellcome & Co. (Australia) Ltd., Victoria-street, Waterloo; p.r. "Wanawong," 27 Thornleigh-road, Beecroft.
1935		Lawrence, Elizabeth Frances, B.A.
1936		Leach, Stephen Laurence, B.A., B.Sc., A.A.C.I., 69 Lithgow-street, Crows Nest.
1924		Leech, Thomas David James, B.Sc., B.E. *Syd.*, P. N. Russell School of Engineering, University of Sydney; p.r. 57 Clanalpine-street, Mosman.
1934		Leech, William Dale, Director of Research, Australasian Food Research Laboratories, Cooranbong, N.S.W.
1936	P 1	Lemberg, Max Rudolf, D.Phil., Biochemist, Royal North Shore Hospital; p.r. 36 Goodchap-road, Chatswood.

Elected.		
1920		Le Souef, Albert Sherbourne, Curator, Taronga Park, Mosman ; p.r. 3 Silex-road, Mosman.
1916		L'Estrange, Walter William, 7 Church-street, Ashfield.
1909		Leverrier, Frank, B.A., B.Sc., K.C., c/o Austral Malay Tin Ltd., Challis House, Martin-place, Sydney ; p.r. Wentworth-road, Vaucluse.
1929	P 14	Lions, Francis, B.Sc., Ph.D., A.I.C., Lecturer in Organic Chemistry in the University of Sydney ; p.r. 31 Chesterfield-road, Epping.
1906		Loney, Charles Augustus Luxton, M.Am.Soc.Refr.E., National Mutual Building, 350 George-street, Sydney.
1927	P 1	Love, William Henry, B.Sc., Ph.D., Cancer Research Department, University of Sydney.
1906	P 2	McIntosh, Arthur Marshall, "Moy Lodge," Hill-street, Roseville.
1891	P 1	‡McKay, R. T., L.S., M.Inst.C.E., Eldon Chambers, 92 Pitt-street, Sydney.
1932		McKie, Rev. Ernest Norman, B.A. *Syd.*, 18 New Canterbury-road, Petersham.
1927		McMaster, Sir Frederick Duncan, Kt., "Dalkeith," Cassilis, N.S.W.
1916		McQuiggin, Harold G., M.B., Ch.M., B.Sc., Lecturer and Demonstrator in Physiology in the University of Sydney ; p.r. 11A Frenchman's-road, Randwick.
1924		Mance, Frederick Stapleton, "Binbah," Lucretia-avenue, Longueville.
1880	P 1	Manfred, Edmund Cooper, Architect, Belmore-square, Goulburn.
1926		Mathews, Hamilton Bartlett, B.A., F.I.S., F.C.I.V., Surveyor-General of N.S.W., Department of Lands, Sydney.
1935		Maze, Wilson Harold, B.Sc., Lecturer in Geography, University of Sydney.
1933		Mears, Arthur Cyril Weeks, A.S.A.S.M. (Electrical and Mechanical Engineering), Engineer Commander, Royal Australian Navy, Navy Office, St. Kilda-road, Melbourne, S.C.1, Victoria.
1912		Meldrum, Henry John, B.A., B.Sc., Lecturer, The Teachers' College, University Grounds, Newtown ; p.r. 98 Sydney-road, Manly.
1929	P 10	Mellor, David Paver, M.Sc., Lecturer and Demonstrator, Chemistry Department, University of Sydney ; p.r. 35 Oliver-road, Roseville.
1928		Micheli, Louis Ivan Allan, M.Sc., Ph.D., Research Chemist, c/o Colonial Sugar Refining Co., Pyrmont.
1926		Mitchell, Ernest Marklow, A.M.I.E. *Aust.*, Civil Engineer, Metropolitan Water, Sewerage and Drainage Board, 341 Pitt-street, Sydney ; p.r. 106 Harrow-road, Bexley.
1922	P 24	Morrison, Frank Richard, A.A.C.I., F.C.S., Assistant Chemist, Technological Museum, Sydney.

Elected.		
1934		Mort, Francis George Arnot, Chemist, c/o Lewis Berger & Sons Ltd., Rhodes; p.r. 16 Grafton-street, Woollahra.
1879		Mullins, John Lane, M.L.C., M.A. *Syd.*, Barrister, 7 Greenknowe-avenue, Potts Point.
1915		Murphy, Robert Kenneth. Dr.Ing., Chem.Eng., A.S.T.C., M.I.Chem.E., A.A.C.I., Lecturer in Charge of Chemistry and Head of Science Department, Sydney Technical College.
1923	P 2	Murray, Jack Keith, B.A., B.Sc.Agr., Principal, Queensland Agricultural College, Gatton, Queensland, and Professor of Agriculture in the University of Queensland.
1893	P 4	Nangle, James, O.B.E., F.R.A.S., F.R.A.I.A., Government Astronomer, The Observatory, Sydney; Room 706, Australia House, Carrington-street, Sydney. (President, 1920.)
1930	P 4	Naylor, George Francis King, M.A., M.Sc., Dip.Ed., Assistant Director, Australian Institute of Industrial Psychology, 12 O'Connell-street, Sydney; p.r. "Kingsleigh," Ingleburn, N.S.W.
1932		Newman, Ivor Vickery, M.Sc., Ph.D., F.R.M.S., F.L.S., Department of Biology, Victoria University College, Wellington, N.Z.
1924		Nickoll, Harvey, L.R.C.P., L.R.C.S., Terrigal, N.S.W.
1935		Nicol, Phyllis Mary, M.Sc., Sub-Principal, The Women's College, Newtown.
1891		‡Noble, Edward George, L.S., Local Government Engineer, 8 Louisa-road, Balmain.
1920	P 3	‡Noble, Robert Jackson, M.Sc., B.Sc.Agr., Ph.D., Biologist, Department of Agriculture, Box 36A, G.P.O., Sydney: p.r. "Warrah," 51 Boundary-street, Roseville. (Vice-President.) (President, 1934.)
1935		O'Connell, Rev. Daniel J. K., S.J., M.Sc., F.R.A.S., Riverview College Observatory, Sydney.
1903		‡Old, Richard, "Waverton," Bay-road, North Sydney.
1930		O'Leary, Rev. William J., S.J., Seismologist, Riverview College Observatory, Riverview, Sydney.
1913		Ollé, A. D., F.C.S., A.A.C.I., "Kareema," Charlotte-street, Ashfield.
1932		O'Neill, John Patrick, F.I.I.A., F.C.I. (*Eng.*), Chief Timber Inspector, Department of Railways, Railway House, York-street, Sydney; p.r. 38 Wilberforce-avenue, Rose Bay.
1921	P 4	Osborne, George Davenport, D.Sc., Lecturer and Demonstrator in Geology in the University of Sydney.
1928		Parsons, Stanley William Enos, Analyst and Inspector, N.S.W. Explosive Department; p.r. Shepherd-road, Artarmon.

Elected.		
1920	P 71	Penfold, Arthur Ramon, F.A.C.I., F.C.S., Curator and Economic Chemist, Technological Museum, Harris-street, Ultimo; p.r. 25 Ramsay-road, Pennant Hills. (Hon. Treasurer.) (President, 1935.)
1933		Penman, Arthur Percy, B.E. *Syd.*, Mining Engineer, 10 Water-street, Wahroonga.
1938		Phillips, Marie Elizabeth, B.Sc. (Hons.), Geology, 20 Kardinia-road, Clifton Gardens.
1935		Phillips, Orwell, "Linlithgow," 4 Wentworth-street, Point Piper.
1938		Pickard, Una Annie Frazer, B.Sc., Microscopist, 5 Malvern-avenue, Croydon.
1919		Poate, Hugh Raymond Guy, M.B., Ch.M. *Syd.*, F.R.C.S. *Eng.*, L.R.C.P. *Lond.*, F.R.A.C.S., Surgeon, 225 Macquarie-street, Sydney; p.r. 38 Victoria-road, Bellevue Hill.
1896		†Pope, Roland James, B.A. *Syd.*, M.D., Ch.M., F.R.C.S. *Edin.*, 185 Macquarie-street, Sydney.
1935		Potts, Charles Vickers, 28 O'Connell-street, Sydney.
1921	P 2	Powell, Charles Wilfrid Roberts, F.I.C., A.A.C.I., Company Executive, c/o Colonial Sugar Refining Co., O'Connell-street, Sydney; p.r. "Wansfell," Kirkoswald-avenue, Mosman.
1918		Powell, John, Managing Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern; p.r. "Elgarth," Ranger's-road, Cremorne.
1927		Price, William Lindsay, B.E., B.Sc., Teacher of Physics, Sydney Technical College; p.r. 130 Provincial-road, Lindfield.
1918		Priestley, Henry, M.D., Ch.M., B.Sc., Professor of Biochemistry, Faculty of Medicine, the University of Sydney.
1893		Purser, Cecil, B.A., M.B., Ch.M. *Syd.*, "Ascot," Grosvenor-road, Wahroonga.
1935	P 3	‡Quodling, Florrie Mabel, B.Sc., Demonstrator in Geology, University of Sydney.
1922	P 8	Raggatt, Harold George, M.Sc., Geologist, c/o Mines Department, Sydney.
1919	P 3	Ranclaud, Archibald Boscawen Boyd, B.Sc., B.E., Lecturer in Physics, Teachers' College, The University, Sydney.
1936		Randall, Harry, Buena Vista-avenue, Eastwood.
1931	P 1	Rayner, Jack Maxwell, B.Sc., F.Inst.P., Physicist to the Department of Mines, Sydney; p.r. 125 William-street, Granville.
1935		Reid, Cicero Augustus, 11 Robertson-road, Centennial Park.
1937		Reuter, Fritz, D.Phil., A.A.I.C., Research Chemist, No. 5, "Wingham," Brighton-boulevarde, North Bondi.
1932		Richardson, Henry Elmar, Chemist, Chase-road, Turramurra.

Elected.			
1933			Roberts, Richard George Crafter, Electrical Engineer, " Redcliffe," Liverpool-road, Ashfield.
1935			Robinson, Albert Jordan, Managing Director, S. T. Leigh & Co. Ltd., Raleigh Park, Kensington.
1935	P	1	Room, Thomas G., M.A., Professor of Mathematics in the University of Sydney.
1928			Ross, Allan Clunies, B.Sc., F.C.A. (*Aust.*), Chartered Accountant (*Aust.*), 54A Pitt-street, Sydney ; p.r. The Grove, Woollahra. (Member from 1915 to 1924.)
1929			Royle, Norman Dawson, M.D., Ch.M., 185 Macquarie-street, Sydney.
1934			Salter, Keith Eric Wellesley, B.Sc., Entomologist, Curator Macleay Museum, The University of Sydney ; p.r. " Hawthorn," 48 Abbotsford-road, Homebush.
1935			Savage, Clarence Golding, Director of Fruit Culture, Department of Agriculture. Sydney.
1920			Scammell, Rupert Boswood, B.Sc. (*Syd.*), A.A.C.I., F.C.S., c/o F. H. Faulding & Co. Ltd., 98 Castlereagh-street, Redfern ; p.r. 10 Buena Vista-avenue, Clifton Gardens.
1933			Selby, Esmond Jacob, Dip.Com., Sales Manager, " Marley," Werona-avenue, Gordon.
1936			Sellenger, Brother Albertus, Sacred Heart College, Glenelg, S.A.
1936			Sherrard, Kathleen Margaret Maria (Mrs.), M.Sc. (*Melb.*), 43 Robertson-road, Centennial Park.
1917			Sibley, Samuel Edward, Mount-street, Coogee.
1938			Sheahan, Thomas Henry Kennedy, B.Sc., Chemist, Shell Co. of Australia, 2 Edward-street, Gordon.
1900			‡Simpson, R. C., Lecturer in Electrical Engineering, Technical College, Sydney.
1933			Slade, George Hermon, B.Sc., Director, W. Hermon Slade & Co. Ltd., Manufacturing Chemists, 23 Rosebery-avenue, Rosebery ; p.r. " Raiatea," Oyama-avenue, Manly.
1922	P	1	Smith, Thomas Hodge, Australian Museum, College-street, Sydney.
1919			Southee, Ethelbert Ambrook, O.B.E., M.A., B.Sc., B.Sc.Agr., Principal, Hawkesbury Agricultural College, Richmond, N.S.W.
1921			Spencer-Watts, Arthur, " Araboonoo," Glebe-street, Randwick.
1917			Spruson, Wilfred Joseph, M.C.I.P.A., F.I.A.P.A., c/o Spruson & Ferguson, Patent Attorneys and Consulting Engineers, 66 Pitt-street, Sydney ; p.r. " Bengalala," Neutral Bay.
1916			Stephen, Alfred Ernest, F.C.S., c/o Box 1158 HH, G.P.O., Sydney.
1914			Stephens, Frederick G. N., F.R.C.S., M.B., Ch.M., 135 Macquarie-street, Sydney ; p.r. Captain Piper's-road and New South Head-road, Vaucluse.

Elected.		
1900	P 1	Stewart, J. Douglas, B.V.Sc., F.R.C.V.S., Professor of Veterinary Science in the University of Sydney; p.r. "Berelle," Homebush-road, Strathfield. (President, 1927.)
1909		Stokes, Edward Sutherland, M.B., Ch.M. *Syd.*, D.P.H. *Irel.*, Medical Officer, Metropolitan Board of Water Supply and Sewerage, 341 Pitt-street, Sydney; p.r. 15 Highfield-road, Lindfield.
1916	P 1	Stone, Walter George, F.S.T.C., A.A.C.I., Senior Analyst, Department of Mines, Sydney; p.r. 14 Rivers-street, Bellevue Hill.
1918		‡Sullivan, Herbert Jay, Director in Charge of Research and Technical Department, c/o Lewis Berger & Sons (Australia) Ltd., Rhodes; Box 23, P.O., Burwood; p.r. "Stonycroft," 10 Redmyre-road, Strathfield.
1918		Sundstrom, Carl Gustaf, Managing Director, Federal Match Co. Ltd., Park-road, Alexandria; p.r. 74 Alt-street, Ashfield.
1901	P 16	‡Sussmilch, C. A., F.G.S., F.S.T.C., Consulting Geologist, 11 Appian Way, Burwood. (President, 1922.)
1919		‡Sutherland, George Fife, A.R.C.Sc. *Lond.*, Assistant Professor of Mechanical Engineering in the University of Sydney.
1920		Sutton, Harvey, O.B.E., M.D., D.P.H. *Melb.*, B.Sc. *Oxon.*, Professor of Preventive Medicine and Director, School of Public Health and Tropical Medicine, University of Sydney; p.r. "Lynton," 27 Kent-road, Rose Bay.
1915	P 3	Taylor, Harold B., M.C., D.Sc., F.I.C., F.A.C.I., Second Government Analyst, Department of Public Health, 93 Macquarie-street, Sydney; p.r. 44 Kenneth-street, Longueville.
1935		Tennant, Thomas Henry, Manager, Government Stores Department; p.r. 2 Borrodale-road, South Kensington.
1919		Thorne, Harold Henry, M.A. *Cantab.*, B.Sc. *Syd.*, F.R.A.S., Lecturer in Mathematics in the University of Sydney; p.r. 55 Railway-crescent, Beecroft.
1923		Tindale, Harold, General Manager, The Australian Gas Light Company, Haymarket, Sydney.
1935		Tommerup, Eric Christian, M.Sc., A.A.C.I., P.O. Box 97, Atherton, North Queensland.
1923		Toppin, Richmond Douglas, A.I.C., 231 Weston-road, Rozelle.
1879		Trebeck, P. C., Church-street, Bowral, N.S.W.
1932	P 7	Trikojus, Victor Martin, B.Sc., D.Phil., New Medical School, University of Sydney; p.r. "Buxton," Tusculum-street, Potts Point.
1925		Tye, Cyrus Willmott Oberon, Director of Development and Executive Officer of the Unemployment Relief Council, Treasury Building, Bridge-street, Sydney; p.r. 19 Muston-street, Mosman.

Elected.		
1921		Vicars, Robert, Marrickville Woollen Mills, Marrickville.
1892		Vickery, George B., 9th Floor, Barrack House, Barrack-street, Sydney; p.r. "Inveresk," Coventry-road, Homebush.
1935		Vickery, Joyce Winifred, M.Sc., Demonstrator in Botany, University of Sydney; p.r. 6 Coventry-road, Homebush.
1933	P 2	Voisey, Alan Heywood, B.Sc., Geologist, St. George's Hostel, West Kempsey, N.S.W.
1903	P 8	Vonwiller, Oscar U., B.Sc., F.Inst.P., Professor of Physics in the University of Sydney; p.r. "Appenzell," Castle Hill, N.S.W. (President, 1930.)
1936		Waine, Cecil Scott, F.C.A. (*Aust.*), Chartered Accountant, 57 York-street, Sydney.
1910		Walker, Major Harold Hutchison, Vickery's Chambers, 82 Pitt-street, Box 1723 JJ, G.P.O., Sydney.
1919	P 1	Walkom, Arthur Bache, D.Sc., Science House, Gloucester-street, Sydney; p.r. 45 Nelson-road, Lindfield.
1903		Walsh, Fred., J.P., Consul-General for Honduras in Australia and New Zealand; For. Memb. Inst. Patent Agents, Lond.; Patent Attorney Regd. U.S.A.; Memb. Patent Law Assoc., Washington; Regd. Patent Attorn. Comm. of Aust.; Barrack House, 16 Barrack-street, Sydney; p.r. "Walsholme," Centennial Park.
1913	P 4	Wardlaw, Hy. Sloane Halcro, D.Sc. *Syd.*, F.A.C.I., Lecturer and Demonstrator in Physiology in the University of Sydney.
1921		‡Waterhouse, Gustavus Athol, D.Sc., B.E., F.R.E.S., F.R.Z.S., 39 Stanhope-road, Killara.
1924		Waterhouse, Leslie Vickery, B.E. *Syd.*, Mining Engineer, Shell House, Carrington-street, Box 58cc, G.P.O., Sydney; p.r. 4 Bertha-road, Neutral Bay.
1919		Waterhouse, Lionel Lawry, B.E. *Syd.*, Lecturer and Demonstrator in Geology in the University of Sydney.
1919	P 3	Waterhouse, Walter L., M.C., D.Sc.Agr., D.I.C., F.L.S., Faculty of Agriculture, University of Sydney; p.r. "Hazelmere," Chelmsford-avenue, Lindfield. (Vice-President.) (President, 1937.)
1911	P 1	Watt, Robert Dickie, M.A., B.Sc., Professor of Agriculture in the University of Sydney; p.r. 64 Wentworth-road, Vaucluse. (President, 1925.)
1936		Wearne, Harold Wallis, 6 Collingwood-street, Drummoyne.
1920	P 39	Welch, Marcus Baldwin, B.Sc., A.I.C., Senior Research Officer, Forestry Commission of N.S.W., 96 Harrington-street, Sydney.
1920	P 1	Wellish, Edward Montague, M.A., Associate-Professor of Applied Mathematics in the University of Sydney; p.r. 15 Belgium-avenue, Roseville.
1921		Wenholz, Harold, B.Sc.Agr., Director of Plant Breeding, Department of Agriculture, Sydney.

Elected.		
1935		Wentworth, William Charles, 17 Wentworth-street, Point Piper.
1881		‡Wesley, W. H., London.
1931		Wheatley, Frederick William, C.B.E., B.Sc. *Oxon.*, D.Sc., B.A. *Adel.*, A.S.A.S.M., 4 “ Rhodesia,” Macleay-street, Potts Point.
1922		Whibley, Harry Clement, c/o Box 1860 W, G.P.O., Brisbane, Queensland.
1909	P 3	‡White, Charles Josiah, B.Sc., Lecturer in Chemistry, Teachers' College, University Grounds, Newtown.
1928		Wiesener, Frederick Abbey, M.B., Ch.M., D.O.M.S., Ophthalmic Surgeon, 143 Macquarie-street, Sydney; p.r. Jersey-road, Strathfield.
1921		Willan, Thomas Lindsay, B.Sc., Field Office, Bhamo, Upper Burma.
1920		Williams, Harry, A.I.C., A.A.C.I., Chief Chemist, c/o The Lanoleen Co., Arlington Mills, Lord-street, Botany; p.r. “ Southerndale,” Burke-street, Oatley.
1935	P 1	Wilson, Ralph Dudingston, M.Sc.Agr., Biological Branch, Department of Agriculture, Sydney.
1935		Wolstenholme, Edmund Kay, “ Petarli, ’ New South Head-road, Double Bay.
1936	P 1	Wood, Harley Weston, Assistant Astronomer, Sydney Observatory; p.r. 4 Ormond-street, Ashfield.
1891		Wood, Percy Moore, L.R.C.P. *Lond.*, M.R.C.S. *Eng.*, “ The Braes,” 71 Redmyre-road, Strathfield.
1906	P 12	Woolnough, Walter George, D.Sc., F.G.S., Department of the Interior, Canberra, F.C.T.; p.r. “ Callabonna,” Park-avenue, Gordon. (President, 1926.)
1916		Wright, George, Company Director, c/o Farmer & Company Limited, Sydney; p.r. “ Wanawong,” Castle Hill, N.S.W.
1921		Yates, Guy Carrington, Seedsman, c/o Arthur Yates & Co. Ltd., 184 Sussex-street, Sydney; p.r. Boomerang-street, Turramurra.

HONORARY MEMBERS.

Limited to Twenty.

Elected.	
1914	Hill, James P., D.Sc., F.R.S., Professor of Zoology, University College, Gower-street, London, W.C.1, England.
1931	Lyle, Sir Thomas Ranken, K.B., C.B.E., M.A., D.Sc., F.R.S., “ Lisbuoy,” Irving-road, Toorak, Melbourne, Victoria.
1915	Maitland, Andrew Gibb, F.G.S., “ Bon Accord,” 28 Melville-terrace, South Perth, W.A.
1912	Martin, Sir Charles J., C.M.G., D.Sc., F.R.S., Roebuck House, Old Chesterton, Cambridge, England.

Elected.	
1935	Murray, His Excellency Sir John Hubert Plunkett, K.C.M.G., B.A., Lieutenant-Governor of Papua, Government House, Port Moresby.
1915	Thomson, Sir Joseph J., O.M., M.A., D.Sc., F.R.S., Nobel Laureate, Master of Trinity College, Cambridge, England.
1922	Wilson, James T., M.B., Ch.M. *Edin.*, F.R.S., Professor of Anatomy in the University of Cambridge; p.r. 31 Grange-road, Cambridge, England.

OBITUARY 1937-38.

Ordinary Members.

1937	Conacher, Charles William Davey.
1892	Cowdery, George Robert.

Honorary Members.

1934	Howchin, Walter.
1930	Masson, Sir David Orme.

THE REV. W. B. CLARKE MEMORIAL FUND.

The Rev. W. B. Clarke Memorial Fund was inaugurated at a meeting of the Royal Society of N.S.W. in August, 1878, soon after the death of Mr. Clarke, who for nearly forty years rendered distinguished service to his adopted country, Australia, and to science in general. It was resolved to give an opportunity to the general public to express their appreciation of the character and services of the Rev. W. B. Clarke " as a learned colonist, a faithful minister of religion, and an eminent scientific man ". It was proposed that the memorial should take the form of lectures on Geology (to be known as the Clarke Memorial Lectures), which were to be free to the public ; and of a medal to be given from time to time as a reward for meritorious contributions to Geological Science.

The Clarke Memorial Medal was established first, and later, as funds permitted, the Clarke Memorial Lectures have been given at intervals.

CLARKE MEMORIAL LECTURES.

Delivered.

1906. " The Volcanoes of Victoria ", and " The Origin of Dolomite " (two lectures). By Professor E. W. Skeats, D.Sc., F.G.S.

1907. " Geography of Australia in the Permo-Carboniferous Period " (two lectures). By Professor T. W. E. David, B.A., F.R.S.

" The Geological Relations of Oceania." By W. G. Woolnough, D.Sc.

" Problems of the Artesian Water Supply of Australia." By E. F. Pittman, A.R.S.M.

" The Permo-Carboniferous Flora and Fauna and their Relations." By W. S. Dun.

1918. " Brain Growth, Education, and Social Inefficiency." By Professor R. J. A. Berry, M.D., F.R.S.E.

1919. " Geology at the Western Front." By Professor T. W. E. David, C.M.G., D.S.O., F.R.S.

1936. " The Aeroplane in the Service of Geology." By W. G. Woolnough, D.Sc. (This Journ., 1936, 70, 39.)

1937. " Some Problems of the Great Barrier Reef." By Professor H. C. Richards, D.Sc. (This Journ., 1937, 71, 68.)

1938. " The Simpson Desert and its Borders." By C. T. Madigan, M.A., B.Sc., B.E., D.Sc. (Oxon.). (See p. 503.)

AWARDS OF THE CLARKE MEDAL.

Established in memory of

The Revd. WILLIAM BRANWHITE CLARKE, M.A., F.R.S., F.G.S., etc.

Vice-President from 1866 to 1878.

The prefix * indicates the decease of the recipient.

Awarded.	
1878	*Professor Sir Richard Owen, K.C.B., F.R.S.
1879	*George Bentham, C.M.G., F.R.S.
1880	*Professor Thos. Huxley, F.R.S.
1881	*Professor F. M'Coy, F.R.S., F.G.S.
1882	*Professor James Dwight Dana, LL.D.
1883	*Baron Ferdinand von Mueller, K.C.M.G., M.D., Ph.D., F.R.S., F.L.S.
1884	*Alfred R. C. Selwyn, LL.D., F.R.S., F.G.S.
1885	*Sir Joseph Dalton Hooker, O.M., G.C.S.I., C.B., M.D., D.C.L., LL.D., F.R.S.
1886	*Professor L. G. De Koninck, M.D.
1887	*Sir James Hector, K.C.M.G., M.D., F.R.S.
1888	*Rev. Julian E. Tenison-Woods, F.G.S., F.L.S.
1889	*Robert Lewis John Ellery, F.R.S., F.R.A.S.
1890	*George Bennett, M.D., F.R.C.S. *Eng.*, F.L.S., F.Z.S.
1891	*Captain Frederick Wollaston Hutton, F.R.S., F.G.S.
1892	*Sir William Turner Thiselton Dyer, K.C.M.G., C.I.E., M.A., LL.D., Sc.D., F.R.S., F.L.S.
1893	*Professor Ralph Tate, F.L.S., F.G.S.
1895	*Robert Logan Jack, LL.D., F.G.S.. F.R.G.S.
1895	*Robert Etheridge, Jnr.
1896	*The Hon. Augustus Charles Gregory, C.M.G., F.R.G.S.
1900	*Sir John Murray, K.C.B., LL.D., Sc.D., F.R.S.
1901	*Edward John Eyre.
1902	*F. Manson Bailey, C.M.G., F.L.S.
1903	*Alfred William Howitt, D.Sc., F.G.S.
1907	*Professor Walter Howchin, F.G.S., University of Adelaide.
1909	*Dr. Walter E. Roth, B.A.
1912	*W. H. Twelvetrees, F.G.S.
1914	Sir A. Smith Woodward, LL.D., F.R.S., Keeper of Geology, British Museum (Natural History), London.
1915	*Professor W. A. Haswell, M.A., D.Sc., F.R.S.
1917	*Professor Sir Edgeworth David, K.B.E., C.M.G., D.S.O., M.A., Sc.D., D.Sc., F.R.S., F.G.S.
1918	Leonard Rodway, C.M.G., Honorary Government Botanist, Hobart, Tasmania.
1920	*Joseph Edmund Carne, F.G.S.
1921	*Joseph James Fletcher, M.A., B.Sc.
1922	Richard Thomas Baker, The Crescent, Cheltenham.
1923	*Sir W. Baldwin Spencer, K.C.M.G., M.A., D.Sc., F.R.S.
1924	*Joseph Henry Maiden, I.S.O., F.R.S., F.L.S., J.P.
1925	*Charles Hedley, F.L.S.
1927	Andrew Gibb Maitland, F.G.S., "Bon Accord," 28 Melville Terrace, South Perth, W.A.
1928	Ernest C. Andrews, B.A., F.G.S., 32 Benelong Crescent, Bellevue Hill.
1929	Professor Ernest Willington Skeats, D.Sc., A.R.C.S., F.G.S., University of Melbourne, Carlton, Victoria.

Awarded.

1930 L. Keith Ward, B.A., B.E., D.Sc., Government Geologist, Geological Survey Office, Adelaide.

1931 *Robin John Tillyard, M.A., D.Sc., Sc.D., F.R.S., F.L.S., F.E.S., Canberra, F.C.T.

1932 Frederick Chapman, A.L.S., F.G.S., Melbourne.

1933 Walter George Woolnough, D.Sc., F.G.S., Department of the Interior, Canberra, F.C.T.

1934 Edward Sydney Simpson, D.Sc., B.E., F.A.C.I., Carlingford, Mill Point, South Perth, W.A.

1935 George William Card, A.R.S.M., 16 Ramsay-street, Collaroy, N.S.W.

1936 Sir Douglas Mawson, Kt., O.B.E., F.R.S., D.Sc., B.E., University of Adelaide.

1937 J. T. Jutson, B.Sc., LL.B., 9 Ivanhoe-parade, Ivanhoe, Victoria.

1938 Professor H. C. Richards, D.Sc., The University of Queensland, Brisbane.

AWARDS OF THE SOCIETY'S MEDAL AND MONEY PRIZE.

Money Prize of £25.

Awarded.

1882 John Fraser, B.A., West Maitland, for paper entitled "The Aborigines of New South Wales."

1882 Andrew Ross, M.D., Molong, for paper entitled "Influence of the Australian climate and pastures upon the growth of wool."

The Society's Bronze Medal and £25.

1884 W. E. Abbott, Wingen, for paper entitled "Water supply in the Interior of New South Wales."

1886 S. H. Cox, F.G.S., F.C.S., Sydney, for paper entitled "The Tin deposits of New South Wales."

1887 Jonathan Seaver, F.G.S., Sydney, for paper entitled "Origin and mode of occurrence of gold-bearing veins and of the associated Minerals."

1888 Rev. J. E. Tenison-Woods, F.G.S., F.L.S., Sydney, for paper entitled "The Anatomy and Life-history of Mollusca peculiar to Australia."

1889 Thomas Whitelegge, F.R.M.S., Sydney, for paper entitled "List of the Marine and Fresh-water Invertebrate Fauna of Port Jackson and Neighbourhood."

1889 Rev. John Mathew, M.A., Coburg, Victoria, for paper entitled "The Australian Aborigines."

1891 Rev. J. Milne Curran, F.G.S., Sydney, for paper entitled "The Microscopic Structure of Australian Rocks."

1892 Alexander G. Hamilton, Public School, Mount Kembla, for paper entitled "The effect which settlement in Australia has produced upon Indigenous Vegetation."

1894 J. V. De Coque, Sydney, for paper entitled the "Timbers of New South Wales."

1894 R. H. Mathews, L.S., Parramatta, for paper entitled "The Aboriginal Rock Carvings and Paintings in New South Wales."

Awarded.

1895 C. J. Martin, D.Sc., M.B., F.R.S., Sydney, for paper entitled "The physiological action of the venom of the Australian black snake (*Pseudechis porphyriacus*)."

1896 Rev. J. Milne Curran, Sydney, for paper entitled "The occurrence of Precious Stones in New South Wales, with a description of the Deposits in which they are found."

AWARDS OF THE WALTER BURFITT PRIZE.

Bronze Medal and Money Prize of £50.

Established as the result of a generous gift to the Society by Dr. W. F. Burfitt, B.A., M.B., Ch.M., B.Sc., of Sydney. Awarded at intervals of three years to the worker in pure and applied science, resident in Australia or New Zealand, whose papers and other contributions published during the past three years are deemed of the highest scientific merit, account being taken only of investigations described for the first time, and carried out by the author mainly in these Dominions.

Awarded.

1929 Norman Dawson Royle, M.D., Ch.M., 185 Macquarie Street, Sydney.

1932 Charles Halliby Kellaway, M.C., M.D., M.S., F.R.C.P., The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.

1935 Victor Albert Bailey, M.A., D.Phil., Associate-Professor of Physics, University of Sydney.

AWARDS OF LIVERSIDGE RESEARCH LECTURESHIP.

This Lectureship was established in accordance with the terms of a bequest to the Society by the late Professor Archibald Liversidge. Awarded at intervals of two years, for the purpose of encouragement of research in Chemistry. (This Journal, Vol. LXII, pp. x-xiii, 1928.)

Awarded.

1931 Harry Hey, c/o The Electrolytic Zinc Company of Australasia, Ltd., Collins Street, Melbourne.

1933 W. J. Young, D.Sc., M.Sc., University of Melbourne.

ISSUED MARCH 17, 1938.

VOL. LXXI. PART I.

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AND
PROCEEDINGS
OF THE
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OF
NEW SOUTH WALES
FOR
1937
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PART I (pp. 1 to 117)
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Containing Presidential Address, Clarke Memorial Lecture, and Papers read from June to August.

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THE HONORARY SECRETARIES.

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GLOUCESTER AND ESSEX STREETS

1938

CONTENTS.

VOLUME LXXI.

Part I.

PRESIDENTIAL ADDRESS

By Edgar H. Booth, M.C., D.Sc., F.Inst.P.

(Delivered to the Royal Society of New South Wales, May 5, 1937.)

Part I. GENERAL.

A feature of the Society's meetings this year has been the large number of papers read. Twice the number of papers accepted during 1935-36 was presented during the past year. This year's volume of the "Journal and Proceedings" is consequently much larger than it has been for the last few years; the cost of this is not, however, reflected in this year's Statement of Receipts and Payments, as this covers the publication of only the first part of this year's volume. The increase will be shown in the financial statement of the year 1937-38, but the surplus which we are carrying forward this year should ensure that the next Council will suffer no embarrassment from the increased cost of Volume LXXI.

The subjects covered in this year's volume are as varied as usual, and we have been pleased to find the authors include not only those on whom we rely to supply a part of our Journal every year, but also many whose work has not previously been published by us. As the principal publishing organisation for scientific works in the State—I think I am justified in saying that, as most of the other organisations publish works only on specialised subjects—we are most gratified to know that the volume of scientific papers, embodying original research, is increasing, while the quality of the work remains as high as ever.

The attendance at our monthly meetings has remained satisfactory this year, and as far as possible, considering the time that has had perforce to be given to the papers to be read—an average of five a meeting—we have arranged talks and exhibits on popular subjects, which have provided an attraction at the meetings for those members whose interests are not specialised.

Four popular science lectures were delivered during the winter months of 1936, and in February, 1937, Mr. G. G. Blake lectured before the Society on "The Electrical Production of Music (Heterodyne Method)".

The example set last year, when the Council arranged for a Clarke Memorial Lecture—the first since 1918—to be delivered, was followed this year, and in April, 1937, Professor H. C. Richards delivered a lecture entitled "The Great Barrier Reef of Australia and its Origin". This lecture was particularly well attended, and it is to be regretted that the Hall of Science House is not sufficiently large to justify a wider advertising of these lectures. The Clarke Memorial Medal was this year awarded to Mr. John Thomas Jutson, B.Sc., LL.B., of Victoria.

The Annual Dinner was again held in David Jones' Auditorium, and was an enjoyable and well attended function, the principal guest being the Hon. D. H. Drummond, Minister for Education.

His Excellency Sir Murray Anderson became the Society's Vice-Patron in August of last year, and it was with deep regret that we heard of his death less than three months afterwards. It is with pleasure that I now announce that His Excellency Lord Wakehurst, who recently arrived in Sydney, has accepted the office of Vice-Patron of the Society.

During the past year the Society has joined with other scientific societies to collect funds for the purchase of a portrait of the late Sir Edgeworth David. I am happy to say that the necessary amount was raised, the commission for the portrait has been given, and it will shortly be hung in the Hall of Science House.

Another important memorial to this great scientist, who was for so long associated with the Royal Society, has been the publication of a joint paper by Sir Edgeworth and the late Dr. R. J. Tillyard. This work, which is entitled "Memoir on Fossils of the late Pre-Cambrian from the Adelaide Series, South Australia", has been undertaken by Messrs. Angus & Robertson of Sydney, who have published the "Memoir" as an expression of their appreciation of the debt Australia owes to Sir Edgeworth David. The publication bears the imprimatur of the Royal Society of New South Wales.

The Society's financial position, as shown by the Honorary Treasurer's report, is satisfactory, and it is gratifying to note that the amount of arrears of subscriptions outstanding has been reduced, through the efforts of our Honorary Treasurer.

A change in the Balance Sheet this year is the omission of the name of The Institution of Engineers, Australia, from the list of sundry debtors. During the past year The Institution repaid the balance of the amount that was lent by this Society to enable the Institution to become a joint owner of Science House.

The library has made steady progress during the year, Mr. H. Williams and Professor J. C. Earl having acted as honorary librarians. Approximately £100 has been spent on binding and the purchase of periodicals, and a new stack of shelves has been purchased to relieve the congestion of the book space which exists in all sections of the library. We hope that we shall, during the coming year, be able to afford to buy another set of shelves of table height, which will enable a much larger number of current periodicals to be shown than is at present possible. It is the desire of the Council to make the library of the utmost use to the members, and (as far as our funds allow) the facilities which it offers are being steadily improved.

It is with regret that I have to record the deaths of the following members :

Guillaume Daniel Delprat, C.B.E., died on 15th March, 1937, aged 81 years. Mr. Delprat was born at Delft, Holland, and in 1872 he went to Scotland, where he served an apprenticeship in engineering during the construction of the Tay Bridge. After acting as manager of the mining section of the Bede Co., Newcastle-on-Tyne, he came to Australia as general manager for the Broken Hill Proprietary Co. Ltd. While holding this position he discovered and developed the floating process of ore separation, which revolutionised the treatment of certain types of ores. He suggested that the iron ore deposits at Iron Knob should be used by an iron and steel industry, and as a result, in 1916 the first blast furnace at Newcastle was blown in successfully.

Mr. Delprat had an international reputation as a metallurgist. He was associated with the B.H.P. as general manager when it was a leading producer of silver-lead and zinc, and was still associated with the company when the Newcastle steel works were planned and installed.

He had been a member of the Society since 1921.

Albert John Fortescue, who died on the 2nd October, 1936, at the age of 66. He was born at Yackandandah, Victoria, and was one of Australia's most versatile and successful inventors. His first invention was the I.X.L. patent automatic poison cart, which was used principally for the extermination of rabbits. More than 10,000 of these carts have been manufactured at the Arncliffe factory of George Fortescue & Sons Ltd., farm implement manufacturers, of which Mr. Fortescue was managing director. He had been a member of the Society since 1920.

Sir Albert Gould, K.B., V.D., died on the 27th July, 1936, in his 90th year. He was born in Sydney, and educated at Sydney University. He followed in his father's footsteps, and became a solicitor in 1870. He practised at Singleton for 27 years, and then moved to Sydney, where the legal firm of Gould & Shaw became one of the best known in the city. In 1882 Sir Albert (then Mr. Gould) was elected for the constituency of Patrick's Plains; he held this seat for 15 years, and was Minister for Justice from 1889 to 1891 and again from 1894 to 1898. In 1899 he was appointed a member of the Legislative Council.

Sir Albert supported the campaign in opposition to the first Federation Bill, believing that justice would not be done to New South Wales. However, once federation had been decided upon, he worked to promote the interests of the Commonwealth and, having resigned from the Legislative Council, he was elected a member of the first Senate. From 1906 to 1910 he was President of the Senate, and he remained a Senator until 1917. For his services to the State and the Commonwealth he was created a Knight Bachelor in 1908.

Sir Albert took an active part in the affairs of the Anglican Church, he was a member of the board of the Royal Prince Alfred Hospital, a vice-president of the Millions Club, and also a prominent Freemason. He had been a member of the Society since 1897.

Walter L. Hammond, B.Sc., died at Wollongong on the 1st March, 1937, aged 56 years. Mr. Hammond was, until shortly before his death, the Headmaster of Wollongong High School. He had been a member of the Society since 1909.

Robert Newby Kirk, died on the 20th August, 1936, aged 75 years. Mr. Kirk was senior partner in R. N. Kirk & Company, and was the Sydney agent of the Broken Hill Proprietary Co. Ltd. He was born in Victoria and came to Sydney when a young man. He joined the office staff of Mr. Jack Weston, who was afterwards appointed Sydney agent of the Broken Hill Proprietary Co., and when Mr. Weston went abroad as London secretary for the company, Mr. Kirk took charge of the Sydney agency and founded the company known as R. N. Kirk & Co.

Mr. Kirk was a director of many companies concerned with mining and allied industries. He joined the Royal Society in 1919.

CHARLES MYLNE MCDONALD, died on the 27th February, 1937, aged 54 years. He was born in Glasgow, and came to Australia with his parents when he was six years of age. He was educated in Victoria, and entered commercial life as a member of the staff of Hicks, Atkinson & Son, of Melbourne. He became the secretary of the Northern Collieries' Association in 1915, being conjointly manager and secretary of the Mineowners' Insurance Ltd. He became chairman of the Northern Collieries' Association in 1923. At the time of his death he was one of the State's leading business men. He was President of the Employers' Federation for seven years, from 1927 to 1934, and in 1934 represented the employers of Australia at the International Labour Organisations' Conference at Geneva. He also served on the coal industry special tribunals appointed under the Industrial Peace Acts of 1920.

Mr. McDonald became a member of the Society in 1936.

CHARLES DUDLEY RYDER, D.Eng. (*Vienna*), Assoc.I.R.S.M. (*Lond.*), A.A.C.I., F.C.S., died on the 20th August, 1936, aged 66 years. Dr. Ryder was born and educated in Austria, and before coming to Australia he carried out various engineering and water supply works in Austria, Poland and South Africa. When he came to Australia he joined the firm of Lohmann & Company, and after the war he turned to assaying and chemical analysis and became consulting chemist to various companies. For several years before his death he was chief chemist to Lewis Berger and Sons. He joined the Society in 1907.

SIR GRAFTON ELLIOT SMITH, M.A., M.D., F.R.S., F.R.C.P., died in London on the 3rd January, 1937, at the age of 65 years. He was born in Grafton, N.S.W., and was educated there and at the University of Sydney; he was the first "M.D." to be trained wholly in Sydney.

During his career at Sydney University he began research in the morphology of the brain, a work which later made him famous throughout the scientific world. Afterwards he went to Cambridge, where he graduated Master of Arts, was appointed a demonstrator, given the research scholarship of the British Medical Association, elected to a Fellowship of St. John's College, and subsequently appointed to examine and catalogue the brains in the Museum of the

Royal College of Surgeons—the largest collection of brains in existence.

Besides being an anatomist of outstanding ability, Sir Grafton Elliot Smith earned distinction as an anthropologist and Egyptologist. He was Professor of Anatomy at Cairo from 1899 to 1908, and founded the Anatomical Museum of Cairo, which is now the greatest in the world of archæological anatomy. He published, in 1912, "The Ancient Egyptians". Later he became Dean of the Faculty of Medicine at the Manchester University, 1908-1918. In 1919 he became Professor of Anatomy in the University of London.

His published works include "The Ancient Egyptians", "The Evolution of the Dragon", "Shell Shock", "Elephants and Ethnologists", "Tutankhamen's Tomb", "The Diffusion of Culture", "The Psychology of Myths", and "The Royal Mummies".

He was a Fellow of the Royal Society, by which he was awarded the Royal Medal in 1912. He was also a Fellow of the Royal College of Physicians, a member of the General Medical Council, and of several foreign learned societies. He was elected an honorary member of this Society in 1928.

Charles Walker, F.C.S., A.A.C.I., died on the 23rd April, 1936, aged 71 years. Mr. Walker was a member of the firm of Walker and Simpson, accountants and estate agents, and had been a member of the Society since 1910.

Ernest Lee Walter, died on the 25th December, 1936. Mr. Walter was the managing director of Oil Search Ltd., and at the time of his death had been a member of the Society for less than a year.

Part II.

A SPECIAL APPLICATION OF GEOPHYSICS: GEOPHYSICAL PROSPECTING.

Introduction.

A Presidential Address to this Society is supposed to deal with some particular section of science with which the retiring President has made himself especially familiar, and one with which, preferably, some of his own published work in the form of original papers has dealt. Consequently, although as a Physicist many sections of that work appeal to me, this portion of my address will be on one not yet covered by a President, and one, moreover, of interest and value (not necessarily including these present remarks) to our community.

The subject of geophysical prospecting, dealing with the location of underground discordancies by means of which concealed structures and formations may be inferred, is not a new one ; magnetic investigations date back well into the last century, and what we might now call "unscientific" work, and speculation, originated even before that. The investigations began to be placed upon a sound basis, so that men fully qualified as scientists were required to conduct them, during the period of the European War (1914-1919) ; and the subsequent development, though secret in most cases, was rapid ; this will be dealt with in greater detail in appropriate sections.

Australia has taken a small, though active, part in this work ; before the war some isolated work was carried out for mining companies by means of the investigation of the spatial variations in magnetic fields ; but the big impetus to research work, and its application, was afforded by the formation of The Imperial Geophysical Survey in Australia in 1928.

This work was carried out in the joint interest of the British Empire Marketing Board and the Commonwealth Government, each of which contributed half the cost ; it was assisted by the formation in England, in 1929, by the Department of Scientific and Industrial Research, of a Geophysical Survey Research Committee, one of the members of which (Professor A. O. Rankine) visited our survey in its second year, and which attached an officer to the Australian survey for liaison purposes after the first year. Up to this, although certain scientific papers were available, the procedure and theoretical methods of interpretation, particularly with regard to seismic methods, were mysterious, as they were applied by private companies which preferred to keep their methods secret.

No trained personnel, scientific or otherwise, was available in Australia, though some of us were familiar with what had been published, and had carried out some tentative experimental work ; no students had yet been trained, although it was known to be absorbing many science graduates of Continental and American universities, and to be resulting in great development of mining areas, old and new. This local survey, of a scientific rather than of an immediate economic nature, gave us an opportunity to see whether the subject should be developed in Australia. The results showed definitely that this should be done.

The Imperial Geophysical Experimental Survey in Australia carried out research work on the several sections of prospecting methods with which we will deal here, namely (*a*) gravimetric, (*b*) magnetic, (*c*) electrical, and (*d*) seismic, the last section not being investigated until a full year after the other work had actually commenced. It may be said here that all these methods are of importance and value in the study of different problems, and that prospecting by all methods except the seismic has been actively continued in Australia since the closing of the Experimental Survey ; the seismic method is one especially suitable for employment in the solving of many Australian geological problems (particularly prospecting for oil fields), but it is the most expensive, and consequently has regretfully been relegated to the background throughout the financially depressed period elapsing since this geophysical work was taken up here.

This preliminary experimental survey of methods was of very great value, by giving Australians an opportunity to see what was being done abroad, by importing apparatus and equipment, by developing procedure suited to our own conditions, and by training a number of men in the science and technique of the subject ; but for the temporary collapse of the economic system in the last year of the survey it would undoubtedly have resulted in the establishment of maintained training centres in our universities to provide the geophysicists as leaders of field parties for the rapid expanse in the utilisation of these methods which would have followed the published report of the survey.*

The methods were recognised as being of great value in the developing of the mining resources of countries overseas, and large sums (in millions of pounds per annum in the United States alone) were being spent on the systematic geophysical investigation of possible fields, resulting in positive results which proved the work to be of economic value fully justifying the expenditure ; our work here had shown that the methods were applicable to Australia, and that the spending of money within the country would result in the production of greatly increased quantities of materials for export beyond the country, a

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* "Imperial Geophysical Survey : The Principles and Practice of Geophysical Prospecting." Cambridge University Press, 1931.

matter of importance to the Commonwealth; the sudden discovery at this stage that all development must cease, that no money was available to earn more money by developing our resources, that it was impracticable to train any more people to employ them at a later date if the world did not go bankrupt in the meantime, set back the proper development here of geophysical prospecting by at least eight years. We may hope that, with the threat of a "boom" period ahead, the training of our own people may be recommenced, and that it will result in the activity that should have been evident throughout the depression, when it would have been of the greatest value.

We were constrained to bring scientists to Australia to act as our leaders in 1928, when the Imperial Geophysical Survey was formed; that was to be expected. We got the benefit of their knowledge and experience. We have done very little in the way of handing on that knowledge and the experience we then gained, or of increasing it, and a considerable amount of the work in Australia at present is being done directly or indirectly by foreign companies; that is wrong.

Mr. A. B. Broughton Edge, B.Sc., A.R.S.M., M.Inst.M.M., was appointed as Director, and came to Australia to take charge of the survey in that capacity; he was assisted by Dr. E. S. Bieler, M.Sc. (of McGill University, Canada) as Deputy Director; both these scientists were experienced particularly in electrical methods. So that electrical methods might be tested in Australia with as little delay as possible, two other scientists, both of whom had had two years' previous experience in South Africa (Shaw and Ferguson), were also brought to Australia; thus this aspect of the work was provided for.

To provide a leader for the gravimetric and magnetic sections, Dr. N. B. Lewis, B.Sc., a graduate of Melbourne and of Oxford, was attached to the British Geological Survey (by arrangements made through the British Department of Scientific and Industrial Research) and had the opportunity of studying and working in England with such men as Dr. McLintock, Dr. Phemister, Captain H. Shaw, and Mr. Lancaster Jones. A considerable amount of reliable and valuable information on this portion of the work had previously been published, so Dr. Lewis returned to Australia fully qualified to take charge of this section and to train assistants.

With the almost complete cessation of activities at the conclusion of the survey Dr. Lewis found other employment, in which he has subsequently so well established himself that he is probably lost to geophysics. Dr. Bieler died in the service in Western Australia in 1929. Messrs. Broughton Edge, Shaw and Ferguson returned to England, as did the scientist attached from the Department of Scientific and Industrial Research, London (J. McG. Bruckshaw, M.Sc.); we read now of the valuable work they are doing abroad, and receive copies of their published papers.

The seismic section was organised by myself in 1929, and R. L. Aston, B.Sc., B.E., A.M.I.E., was appointed leader. Even with the short time available to this section it carried out much valuable research work, and made available information which would have enabled this method to have been applied in Australia on an economic basis. At the conclusion of the survey the results were published and made available to the world, together with those of other sections in the book to which reference has already been made; the section was disbanded; Dr. Aston is now a lecturer in civil engineering and surveying at the University of Sydney.

The rest of the workers were scattered, some to find other occupations, one or two (two, I think) to do some occasional applied geophysical work for Australian interests; with one exception.

The New South Wales Government showed great foresight in appointing to its staff of the Geological Survey, The Department of Mines, a young graduate in Physics of the University of Sydney, J. M. Rayner, B.Sc. He was then attached for training and experience to the Imperial Geophysical Experimental Survey, and had the opportunity of working with the various field parties and studying the theory and application of the methods employed; owing to the death of Dr. Bieler, the responsibility came to him of preparing the section of the report on the "Electromagnetic Method" of prospecting. When the field work was finished and the report was written and published, Mr. Rayner was retained, mainly for work on geophysical prospecting, as an officer of the Geological Survey, and, with the consent of the University of Sydney, I was appointed to act as Consultant.

Thus in New South Wales alone may the work of the Experimental Survey be said to have continuity; and, mainly through the activities of Mr. Rayner, much field work has been done in gravimetric and magnetic surveys in New South Wales, and some in other States ; and his services have now been made available as Consultant Geophysicist for the present big Commonwealth undertaking, the Aerial, Geological and Geophysical Survey of North Australia.

Certainly, research work has continued in some of our universities ; but it is the training of young scientists to carry on with research work and with its applications that is now urgently required, so that Australia will not have to begin all over again at a later date ; we have just had the opportunity (which still exists) of placing them with the Commonwealth survey ; we have not at any university in Australia the machinery for giving them the qualifying training. (One year, 1931, a course was conducted at the University of Sydney by myself, for the Extension Board ; this was very well attended, and all those who passed and were available were asked to apply for consideration as members of the present survey.)

Before considering what work has been done in the intervening period, as set out on page 32 and subsequent pages, we will outline briefly the principles underlying the different methods. This is a Presidential Address to an audience with varied interests in science, so that I will do no more than indicate the nature of the instruments employed, how they are used, and the conditions for which they are most suitable.

As it is a method of great precision, in which mathematical treatment is most certainly applied in the interpretation of results, we will examine first of all :

THE GRAVIMETRIC METHOD.

We may take it as an experimental fact that all matter attracts all other matter ; and that, whatever may be the nature or location of the material, the force of attraction between two masses is proportional to the product of their masses, and inversely proportional to the square of the distance from the centre of mass of the one to the centre of mass of the other. This is generally expressed as " Newton's Law of Universal Gravitation ",

$$F=\frac{GM_1M_2}{d^2}$$

where G is the universal gravitational constant.

Let us imagine our Earth as a perfectly uniform sphere, with its centre of mass at the geometric centre, and not rotating. Then the mass of the Earth is, say, the mass M_1 of the equation ; if our mass M_2 be some small mass at the surface of the Earth, then the distance " d " is the radius of the earth, being the distance from centre of mass to centre of mass, about 4,000 miles. Here our M_1 is fixed, d is fixed, G is a constant, so that $F \propto M_2$. Taking M_2 (our test mass) as being 1 gramme, then F is found to be approximately 980 dynes ; we express this information, that the pull on the gramme mass is 980 dynes, by saying that the " gravitational intensity " at that place is 980 dynes per gramme. Imagine three axes at right angles at this place—directions OZ vertically upwards, OX towards the north, OY towards the east. What do we mean by " vertically upwards " ? Definitely, in the line of action of the gravitational pull on our test mass, but in the opposite direction ; so that in the case of our *perfectly uniform* non-rotating sphere the vertical is the prolongation of the radius, and the OX-OY axes form a plane at right angles to the vertical, which constitutes a " horizontal surface " at that point.

If we go further up the OZ axis, d increases, so F decreases, and we have a decrease in the value of the gravitational intensity ; we have a " gravity gradient " in the OZ, or vertical direction. Going in the OX or OY direction, if we continued in *straight lines* we would be going in a tangent plane to the uniform sphere, and thus getting further and further from the centre, and hence we could say, with this space rate of change in gravitational intensity, that we had gravity gradients in those directions ; but if we took our OX and OY axes always to be at right angles to the vertical (OZ) from *point to point*, then OX and OY would be curved lines, circles in this particular case. (An area, however big, which is at every point at right angles to the vertical at that point, is called a " level surface ".) Here, then, we would have no gravity gradient in the north or east directions.

The Earth is *not* a perfectly uniform sphere, and it is rotating about an axis. A force is required at the surface to constrain our " test mass " to move in the circular path, the radius of which decreases as we go from the equator to the pole ; also the distance d decreasing as we move from equator to pole means an increase in the value of F. So that, depending on where we stand with our test mass, we have to record a gravity gradient and a change in the gravity gradient as we move northward, even if we are not concerned with local irregularities in the earth's density and local variations in its figure ; here in the southern hemisphere we are going towards the equator as we go northwards, and hence this ordinary or "Normal Northward Gradient" has a negative value. The gravitational intensity here is about 980 dynes per gramme ; we are interested in, and measure, changes as small as one million-millionth of that in a horizontal centimetre ; so we adopt as a unit of gravity gradient an Eötvös (or Eötvös unit), which is 10^{-9} dyne per gramme per horizontal centimetre. The "normal northward gradient" here (lat. 30° S.) is 7 Eötvös, usually written 7E.

Apparatus has been devised (the torsion balance and the gradiometer, for example) which enables us to measure the gravity gradient at any place where we set it up ; we usually find that the gradient is *not* 7E, nor is it *northwards*—a "positive mass" such as a tree, building or hill will give a supplementary pull in that direction which increases in the direction towards it ; a valley or other depression might be regarded as a "negative mass".

We can correct our observed gravity gradient at a place for our calculated normal northward gradient there ; we can contour closely (by "dumpy" or other levels) the ground in the immediate vicinity, and thus calculate and apply a correction for surface irregularities (out to 100 feet probably) ; we can calculate, after survey or by employing surveys of the district made previously, for the effects of embankments and cuttings, river beds, small local hills, and so on ; and we can calculate the effects of larger and more distant obvious irregularities if necessary ; if nothing is left over, if we then have no unexplained gravity gradient, then we do not know that everything unseen is perfectly uniform in its density or distribution, but only that the effects have "balanced out" at that particular place.

Moving on to another station on the traverse, the same procedure is followed. And thus we have a zone of survey area dotted with a number of places (not strictly *points*, because we are measuring gravity *gradients* there) at which we know the change in gravity pull per centimetre, both in magnitude and in direction. If we put arrows at those places, pointing in the direction of the gravity gradient at each station and of length equal to its value, we have a picture which is of immediate qualitative significance to the geophysicist. For example, crossing a buried valley of denser rock filled in and concealed by less dense material, the gravity gradient might be zero (pulls balanced) at the centre, but increasing as we moved in either direction towards the denser buried valley edges "rising" towards the surface. The arrows in general "point" to denser buried mass, increasing in length as we approach it, always with the provision that over it, or between equivalent mass distributions, we will be in a position where the gravity pulls are balanced and hence we get a zero effect.

This explains the general principle; you may consider that the setting up and adjustment and reading of the instrument present difficulties; they do, but we can train intelligent people to carry out those duties, without their fully understanding what it is all about, provided this work is supervised. You may consider that the correction for normal northward gradient, for terrain and topographical effects, and the first calculations and plotting of corrected gravity gradients present difficulties; they do, but they can be carried out by young science graduates, who *do* understand what they are doing, and who have the necessary training in geophysics. You may finally (if you get that far) consider that the interpretation (by a set of mathematical calculations, involving common sense and experience also) of these plotted results presents difficulties: it does, and we require senior and experienced and well-read geophysicists to apply their knowledge. Then the results are there, positive or negative (the geophysicist will not give you what is there merely because you are a public company and want it), as the case may be. The results are correct; the interpretation might be faulty (though it is hard to err far, except by carelessness), but even that can be depended upon if we have trained people. Why not train the men, spend the relatively small sums required for the survey, and know what you are doing before you dig holes in the ground?

This is one method, admirably suited for the investigation of many problems, when variations in the density of surface and buried materials are present; it is not very practicable in rough hilly country, when the corrections (with their introduced errors) may be great. Another method, very generally employed, on account of its cheapness and speed, is:

THE MAGNETIC METHOD.

This method depends on the fact that all rocks and soils either contain or do not contain magnetic material. The contrast between those that do and those that do not, and relative variations in magnetic content amongst those that do, enable us to note their separation in concealed three-dimensional space.

In the early days much work was done by means of the " Dip Circle ". You are all familiar with compass needles—thin pieces of steel, usually shaped like arrows, that are balanced and pivoted so that they are free to swing in a horizontal plane and " point " in the direction of magnetic north at the place where the observation is made. You know that, in general over the world surface, magnetic north is not the same direction as true north : there is an angle between the magnetic meridian and the geographic meridian which is called the magnetic declination at that place (some 9½ degrees east in Sydney). When the needle is supported at its centre of gravity, so as to be free to swing in any plane, then not only does it lie in the magnetic meridian, a plane about 9½ degrees east of north, but here the South Pole " dips ", so that the needle also lies in a plane inclined at about 62½ degrees to the horizontal : there is in Sydney, *in round figures*, a " magnetic dip " of about 62½° S. ; the needle, taken as approximating to a line, or more correctly the axis of the needle, lies in the direction of the magnetic field where it is freely swung. " Dip circle " work depends on that phrase " *in round figures* " : I have taken students with a dip circle over Paul's Grounds behind the Physics School at the University, and, in making practice traverses, we have noticed departures from the " approximately 62½° S." of as much as 3° ; amongst other things, variations in magnetic contents of materials in the vicinity will alter the value (in magnitude and *in direction*) of the magnetic field ; the dip circle shows this change in direction, if present in the vertical plane. For this purpose it is not necessary to have the needle free to swing about any axis, as by a preliminary reading and adjustment it may be arranged that the needle, free to swing about a horizontal axis, does so in the magnetic meridian.

Local variations in the field cause variations in the dip as read ; the local magnetic anomalies in Paul's grounds are probably due largely to old rubbish dumps containing iron residues, and to buried water mains.

Probably the first to think out this method of geophysical prospecting was Freiherr Von Wrede; Professor Robert Thalen published a work in 1879, "On the Examination of Iron Ore Deposits by Magnetic Measurements"; and magnetometer measurements, measuring the variations in intensity of the earth's magnetic field, instead of variations in "dip", were made with greater certainty, and steadily improving methods and instruments from then on.

The Swedish scientists took the lead in the development of this method; I think they are still the leaders in this method, and in certain sections of the electrical processes, operating by Swedish companies throughout the world, and carrying on research work and training students in their own land. Professor Nordenström, of Stockholm, wrote as far back as 1899: "It is astonishing that people in these countries"—European countries other than Sweden—"have not already learned to appreciate the great advantages which are offered the practical miner by the use of magnetic instruments."*

At that date the German peoples, who have gone so far in this direction since, had done very little—I can find no record of published work beyond comments on the published work of Professor Thalen.

References to Swedish literature, published at the conclusion of the last century, show that the main instrument used was the Thalen-Tiberg magnetometer (manufactured by J. Fr. Berg, Stockholm); reference to the report of the Imperial Geophysical Experimental Survey (on page 180) shows that we bought for, and used for a time in the survey in 1928 ". . . and also a Thalen-Tiberg magnetometer, made by Berg of Stockholm".

We employed with that survey, and preferred, a type developed by the Germans, a type referred to as a "Schmidt magnetic balance"; ours were manufactured by Askania Werke A.G. of Berlin, and most of the magnetic surveys carried out in Australia have been done with instruments of that type, measuring variations in the vertical component of the earth's magnetic field. In the present Commonwealth survey, both horizontal and vertical magnetometers ("variometers") of this construction are being employed; instruments, excellent ones, are now manufactured in England.

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* "The Most Prominent and Characteristic Features of Swedish Iron Ore Mining." G. Nordenström (London, 1899).

These magnetic variometers are essentially magnetic balances, in which two permanent magnets mounted in parallel constitute a beam, which can be lowered, like an ordinary physical gravity balance, on to quartz knife-edge contacts on quartz plates. By means of adjusting masses on screws the beam can be made approximately horizontal for a " base station " in a district. The equilibrium is a balance of two sets of torques—the magnetic torque (due to the attraction to the ground on, say, the south polar end and the repulsion from the ground on the north polar end) and the opposing gravity torque (due to displacement of the adjusting masses so as to make the beam tend to tilt in the opposite sense).

On moving to another adjacent station the gravity torque will remain unchanged, whilst the magnetic torque will have changed if the component of the magnetic field has altered. With instruments such as these, extremely small variations in the magnetic contents of the earth's crust can be detected, such as are due, for example, to a change from shale to granite hundreds of feet below ground level; whilst rocks rich in magnetite, such as basalt, are readily mapped as dykes, or in the old leads along which they have flowed.

With the vertical variometer changes as small as two parts in 100,000 of the earth's field may be measured ; it is " changes " that we are hunting for, so that we are not concerned with the absolute value of the field or of its components.

With this method the physicist (aided by the geologist naturally, as geophysical prospecting is always a combined attack by geologist and physicist) can quickly and cheaply plot the local magnetic variations over a considerable area, and deduce valuable information as to the rock distribution ; in the early days it was only of service in plotting the presence and boundaries of larger masses of iron ore—now we plot any not-too-complicated underground feature by means of the slight variations in small (often minute) quantities of magnetic material distributed through them.

In many cases we can get all the preliminary information we require by a single, quick magnetic survey with a vertical component magnetometer by itself ; in other cases additional information supplied by the horizontal component instrument is of great value ; and we can always check up and get further information by employing other methods on small zones which the large area magnetic survey has shown to be worth further investigation. Eugene Haanel, Superintendent of Mines, Canada, published in 1904 a book, actually a paper read in 1903 at the annual meeting of the Canadian Mining Institute, and titled " On the Location and Examination of Magnetic Ore Deposits by Magnetometric Measurements " ; whilst objecting to the title, we find that Canada at this period was fully alive to the value of geophysical prospecting for iron ores—" In the hands of experts " (italicised), " furnished with such instruments, the Swedish methods yield data from which magnetic iron ore bodies may be located, and in many cases their strike, direction of dip, and depth below the surface may be calculated." Canada has gone far since then, both in the use of the methods and in research work (notably at McGill University, whence came Dr. Bieler as Deputy-Director of our Experimental Survey in 1928) ; and I would emphasise that the magnetic method has gone far beyond the stage discussed in Haanel's book—we can still with ease locate magnetic iron ore deposits, but we employ the method, working with instruments of much greater sensitivity, to locate variations in structure, where the slight variations in magnetic content would have been unobservable with the earlier instruments ; we are not so much interested in hunting the iron ore (a simple matter) as in locating possible oil domes, deep leads where we may find tin or gold, faults where gold and other valuable metals may be found, underground water channels ; the problems which may be solved by the magnetic method are varied, as in general it is not the otherwise negligible iron content that interests us.

Mining companies and prospecting companies are alert to the value of this cheap method of investigating their holdings, and are willing to buy instruments and employ our graduates ; I could have placed nine students over this last year on direct request ; we have no trained men free and available for the work.

The Electrical Methods.

There are many electrical methods in use, and modifications of each system. In some cases the concealed material sends out its own signals, which are detected electrically at the surface ; in others, variations in the electrical properties of substances enable us, by suitable employment of electrical methods on the surface, to note and translate their peculiarities. Electrical conductivity is an important factor.

The Imperial Geophysical Experimental Survey investigated five of these methods, and their results (together with the theory of the processes and descriptions of the instruments and procedure) are clearly set out in the Report; very little geo-electrical work was done in Australia in the intervening years until the commencement of the present Commonwealth survey, except by overseas companies working on contract for mining concerns.

(A) Natural Earth Potential Measurements.

This is the self-signalling method referred to above, and is only applicable when chemical changes are going on in buried ore bodies. For example, sulphide ore bodies of a pyritic character may lie partly below the water-table level, so that their lower portions are in a water-saturated soil, whilst the upper parts are in unsaturated soil, through which percolates to the lower level rain water containing dissolved air. Electro-chemical changes take place, so that the system acts as a large electric cell, and an electric current runs from top to bottom through the ore body, and from below to the top externally through the surrounding soils.

To detect a pyritic ore body of this nature, all we require to do is to pick up the surface electric signals. This is most readily done by plotting on the surface equi-potential curves (lines joining points between which there is no electrical difference in potential), employing a portable potentiometer capable of recording differences in potential of $\frac{1}{500}$th volt. The closed curves thus formed "ring" the buried ore at the ground level, so that, apart from corrections (if necessary) for changes in surface level, the body may be expected immediately below the centre of the closed curve system. There are traps in the interpretation of these results: for instance, electro-chemical action may be due to the presence of anthracite coals and graphite, or peat bogs. Here we may consider a very important point—how are we to make contact with the ground (in this and certain other methods) so as to establish the fact that the two points of contact are at the same potential? It is essential to employ what are known as "non-polarising electrodes" for our earth contacts otherwise we may actually be introducing new small cells by and at the very contact of detector and ground, sufficient to upset and even nullify all readings. The type which was introduced by the Imperial Geophysical Experimental Survey (hereafter referred to as the I.G.E.S.) after trials with the old " Schlumberger " type and modifications is as follows (this is the type at present in use) : A small earthenware pot, glazed externally, has its base closed by a porous earthenware end. This pot has an upper and lower chamber, separated by a porous earthenware partition, the lower chamber being filled with a " copper sulphate jelly ", made by soaking sheets of gelatine in a cold concentrated solution of copper sulphate, melting them, and pouring the hot solution into the lower chamber until, when closed by the porous plug, that space is completely filled by the cold jelly without any air space or bubbles. The upper chamber has fixed into it a tube (about half an inch in diameter) of electrolytic copper, the remainder of this chamber and the contained part of the tube (which is drilled for that purpose) containing a saturated solution of copper sulphate and some extra crystals of copper sulphate ; this solution has a little (about 2%) gelatine added to it.

With two identical " contacts " of this nature, no variation in potential between contacts is introduced ; the description is given here as an illustration of what may appear as small details of knowledge and experience, but which are of fundamental importance ; we have also accumulated much information with regard to the nature of contacts, cross-checking of stations, preservation of electrodes, and so on, which is available to students, whereas private companies naturally enough wish to keep this information to themselves. These pots are now being manufactured in Australia, and made up into non-polarising electrodes as required.

(B) Observation of Surface Potentials.

The second group depend on observation of surface potentials, when direct or alternating current is sent into the ground between a pair of earthed electrodes. Here we depend on differences in conductivity, great or small, between materials in the earth's crust in the area in which the survey is being made. The resistivity of rocks and minerals varies enormously, ranging from the order of 10^{-4} ohm cm. for pyrrhotite, pyrite, galena and other relatively good conductors, down to the order of 10^{6} ohm cms. for igneous rocks, gneisses and crystalline schists of ordinary physical character. Even with the relatively small time spent by government observers on electrical investigation in the field in Australia, a great amount of valuable information has been obtained by them, and is available, concerning the resistivity of materials *in situ.*

Different electrical methods have their advantages or disadvantages, depending on local conditions. We may, in accordance with practice, subdivide the methods of this group and consider them in three parts : (i) Resistivity methods, (ii) Equi-potential line methods, (iii) Potential-ratio method.

Type (*i*) (*Resistivity methods*) may be understood by reference to what is usually known as the "Gish and Rooney" method, so called after the two scientists attached to the Carnegie Institute at Washington. This is a four-electrode method, the two outer electrodes along a linear traverse establishing a difference in potential (D.C.) so that a current flows through the ground, whilst the two inner electrodes are employed to measure the difference in potential then existing between their points of contact. The four electrodes are spaced so that the three inter-electrode distances are equal ; and, by means of a simple equation due to Wenner,* the average resistivity (ρ) of a block of ground to a depth approximately equal to the distance apart of two electrodes may be calculated, in terms of the distance apart (a) (cms.) of two electrodes, the difference in potential between the two central electrodes (P) (volts), and the current (I) (amperes) flowing between the current-input electrodes. (This equation is $\rho=\frac{2\pi aP}{I}$, ρ then being in ohm cms.)

In practice this method is particularly valuable in determining the distance from surface level to a lower level of material of different conductivity ; the electrode spacing is gradually increased, and resistivity calculated and plotted against electrode separation : a change in the slope of the line indicates the discontinuity in resistivity when the current flow through the lower formation becomes of sufficient importance to affect the readings, thus giving both information as to its existence and its approximate depth. The electrodes for this purpose are usually probes spiked, or driven, into the ground.

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* Bureau of Standards Bull., Vol. 12, p. 469 (1916)

This method, as with other methods also, has its drawbacks: the equation given above requires that the ground should be homogeneous and level; in many cases variations in surface resistivity from place to place may be great, or the departure from level conditions may be such that it is not practicable to apply simple corrections; as in any other method, it is necessary to know the conditions which make its employment reasonable, and to be experienced in the interpretation of results. It is a relatively cheap and simple method, the apparatus is robust, and in any applied geophysics we first consider whether the simpler, quicker and more economical methods will give us satisfactory results, before going on to the more complicated methods requiring larger staffs and more expensive equipment.

Depths down to 300 feet have been investigated successfully by this method in Australia.

Type (ii) Equi-potential Line Methods. As its name implies, in these methods an endeavour is made to plot on the map equi-potential lines, a current being passed into the ground through the underlying materials by means of electrodes. These electrodes might be single positive and negative metal pegs driven in, or as is more usual, multipoint electrodes making, both for positive and negative terminals, several adjacent points of contact. Linear electrodes are also employed, forming really an extension of the multipoint system.

Either direct or alternating current may be employed. Dealing firstly with direct current, the multipoint electrode may consist of a length of bare wire pegged on to the ground, sometimes in the form of a set of lines radiating from a common centre, sometimes in the form of a rectangle with diagonals—the object being to decrease as much as practicable the resistance at the point of entry and emergence of the current. The two multipoint electrodes may be a mile apart, and each multipoint, positive or negative, may spread over a circle of radius 100 feet or more. The difference in potential applied between the electrodes is naturally dependent upon the resistivity of the ground, and the distance apart of the electrodes.

The current will flow better through materials of higher electrical conductivity; equi-potential lines being at right angles to lines of current flow will therefore appear to "dodge" concealed materials of higher conductivity than the surrounding material; that is, equi-potential lines would be crowded together over relatively bad conductors, and spread apart over relatively good conductors. (The actual distance apart would of course depend on the steps chosen arbitrarily between increasing or decreasing potentials of lines.)

Using direct current, equi-potential points, and thus lines, may be located accurately and the actual potential difference from line to line measured ; points are readily picked up, the required direction of movement of the exploring contact being indicated by the direction of movement of the galvanometer in the circuit between contacts. Non-polarising electrodes (described on p. 20) are used, because good earth contacts are very important. In practice, the direction of the current is regularly reversed, so as to eliminate the effect of natural earth currents, which will in general be unidirectional, or will not change with a uniform frequency. In demonstrating this method in the University grounds, great difficulty was experienced on account of the big natural earth currents there existing : we could watch the starting and stopping of trams within a big zone, as sufficient current found its own way home instead of using the tram rails. In general, this effect is overcome by the regular reversal of the current applied between our electrodes.

Employing alternating current, equi-potential points are detected by sending in the current with an alternation which will produce an audio-frequency hum in a headphone connecting the two exploring electrodes when a potential difference exists between them. These electrodes are pointed steel probes, which are stuck into the ground—one being used as a search probe. An amplifier set is used, carried on the back of the explorer, so that he forms a mobile unit as he moves about (over some sixty feet) sticking in the steel electrode ; he searches for places of no sound, or, in practice, of minimum sound. That is one of the disadvantages of the A.C. method : currents are also induced in all conducting material in the vicinity, and the secondary fields thus generated may differ in phase from the primary field, so that we never get continuous null points. This need not be a serious disadvantage unless we are working in an area of high conductivity, and modifications of the method allow considerable compensation to be made for this secondary effect. It is a speedy and convenient method for many types of work, so that the added disadvantage of not knowing the potential step from line to line may often be disregarded.

Equi-potential lines being thus plotted, regions of high or low relative conductivity are disclosed by an examination of the departure from parallelism of the lines. These lines, even in a uniformly conducting ground, would appear as circles on the map in the vicinity of point input electrodes; hence the area examined is so far removed from the input electrodes that the arcs of the circles approximate to straight lines. Taking the distance apart of input electrodes as l, exploration would be confined to a rectangle the sides of which commenced about $\frac{1}{6}$l from either electrode, and the width of which is about $\frac{1}{3}$l, giving an area $\frac{2}{3}$l × $\frac{1}{3}$l.

Where the current is sent in through long parallel bare leads, pegged regularly, the equi-potential lines in a uniform conducting material would be parallel to those input leads, and variations in conductivity would be observed as before—a crowding together indicating a poorer conducting zone, and conversely.

This method is not now much used, on account of the extra information obtained for the same work from the potential ratio method.

Type (iii) Alternating Current, Potential Ratio Method. In the last section, dealing with the plotting of equi-potential lines when employing alternating current, reference was made to the fact that secondary effects caused the introduction of phase differences between two points, so that two points might only be momentarily at equal potential during each cycle, and the headphones detected positions of minimum sound and not silence. The potential ratio method actually makes use of information obtained from a consideration of these introduced phase differences, and enables equi-potential lines to be drawn accurately.

As in the last method, an alternating current is sent through the ground, either through point or line electrodes. The search-system consists of three steel probes, equi-spaced from one another along the line traverse being made; these two equal length earth circuits form two adjacent sides, AD and DC, of a four arm system, which may be represented *diagrammatically* by the sides of a diamond network, the opposed adjacent sides, AB and BC, being in the instrument (the ratiometer) carried by the operator. This ratiometer is a device by which resistance and capacity in AB, and resistance and capacity in BC, may be individually and separately varied. The bridge is " balanced " by varying these resistances and capacities until an exact balance of potential and phase between B, and D (the midpoint on the ratiometer system, and the central probe electrode) is obtained; this is observed by a headphone and amplifier set introduced between B and D, a condition of silence of the hum note being obtained. When this adjustment of resistances and capacities has been effected, then the potential drop between the first test electrode (A) and the central one (D), and the potential drop between the central electrode (D) and the third one (C) are directly proportional to the impedances introduced in the corresponding adjacent balance arms AB and BC.

Not only is the relative drop in potential from point to point along a traverse thus mapped, but also the phase difference from point to point, that also being readily calculated in terms of the balancing resistances and capacitative reactances of the two arms. One particular advantage of this method is that it may be used where the A.C. equi-potential line method fails on account of the presence of good conductors introducing such big phase differences that equi-potential points are uncertain. In such cases it is only necessary to run traverses, using the ratiometer, over areas where such supplementary information is required. Progressive total change in phase being plotted against distance along the traverse, the conducting bodies are indicated by peaks above the bodies; further, the potential at points along the traverse may be calculated and plotted in terms of an arbitrarily assigned commencement potential.

A considerable amount of experimental information, supported by theoretical investigations, is available concerning the forms and relations of phase and potential curves over conducting bodies. In particular, the phase curve gives information not only with regard to the presence of the bodies of marked difference in conductivity, but also as to their dip.

The modern instrument is now calibrated and graduated so that potential differences and phase differences are read directly; the operator wears the headphones, carries the amplifier on his back, and the ratiometer slung in front so that he can make the necessary adjustments and readings, and forms a mobile unit for quick work.

The method is also employed for the complete survey of a field, as a knowledge of potential changes along traverses reticulating the area permits of the drawing of equi-potential lines upon it.

(C) Electromagnetic Methods.

In an early section of this address (pp. 16, 17) the investigation of the field by means of observations of variations in magnetic intensity, horizontal and vertical, was considered. In the vicinity of a conductor carrying a current there is a magnetic field, so that if a magnetic survey were made of an area containing some conducting but non-magnetic bodies (which therefore would not be apparent), and then a direct current were passed between electrodes in the ground and a new magnetic survey made, the magnetic field above the conductors particularly would be found to have altered and, provided the change were sufficiently marked, the conductors could thus be mapped. Imagining a horizontal conductor well beneath the surface, the change would be practically entirely in the horizontal component of the earth's field above it.

If, instead of passing a steady current between electrodes, an alternating current were sent through the ground, then the secondary (horizontal) magnetic field thus induced would also alternate with the frequency of the current alternation, but not necessarily in phase with it. This would not, of course, affect the magnetometer, but that instrument could be replaced by a vertical search coil connected to a microvoltmeter, which would indicate the value of the secondary field by the induced e.m.f. thus read.

The current in the ground can itself be induced, instead of introduced between electrodes, and this is the method adopted in general practice. This is not a full discussion of methods, but a summary of the principles underlying those most commonly used and of greatest importance and value to us in Australia, so we will consider here in outline the procedure and theory for one group of methods: a horizontal loop method.

A rectangular circuit of *insulated* wire may be laid out on the ground, to include an area of, say, one-tenth of a square mile (a square of sides one-third of a mile is a reasonable zone). Through this is passed an alternating current (of a few amperes) of reasonably frequency: it may be tens of thousands per second, down to a few hundred per second (500∼ is common, and a generally useful frequency). The electromagnetic field associated with this is, well away from the wires themselves, practically a vertical alternating field; this, cutting the conducting ground and bodies of greater conductivity if there present, induces currents with which will be associated a secondary field, predominantly horizontal. So that, in general, in the zone enclosed by the wires, the field will be one compounded of the two simple harmonic oscillations at right angles, varying in phase and component amplitudes from point to point. Such a combination will give an elliptical compounded oscillation, with straight lines and circles as particular cases; and, the major and minor axes being at right angles (we will not here concern ourselves with variations from this), the inclination of the major axis to the vertical, the relative values of major and minor axis, and the orientation of the plane of the ellipse, can all be determined by using two search coils, and are all of importance to us. We call the angle between the plane of the ellipse and a horizontal plane the "dip" of the electromagnetic field, whilst by "the strike" is meant the direction of the line of intersection of the plane of the ellipse and the horizontal plane, with regard to magnetic north.

In the Bieler-Watson method, and modifications which have been introduced by Australian research workers, the detecting system consists of the two search coils fixed with their planes at right angles to one another. The system is capable of being rotated about a horizontal, and about a vertical axis; and, in the simplest case, the comparison of major and minor axes is made by having a fixed number of turns in the "vertical" plane joined in opposition with a variable number of turns in the "horizontal" coil, through an amplifier and headphone. The system is correctly oriented by experimental balance, as it can be rotated about its axes, and the required number of balancing turns introduced into the "horizontal" coil step by step by movable contacts. A fuller discussion of the method and its modifications would be out of place here, but from this brief explanation it will be seen that it is practicable to obtain dip and strike of the ellipse, and the ratio of major and minor axes.

With this method, it does not matter if the surface layer is a non-conductor—if a conducting body lie below that layer, a current will be induced in it; that is particularly valuable also if the surface is frozen. If no conducting body or layer, within a few hundred feet, were present, there would be no induced current, and so no resulting secondary magnetic field; the magnetic field would then be entirely vertical, and the minor axis of the ellipse would vanish—the vertical field would become weaker as we advanced further from the conducting wires to the centre of the circle. The better the conductor in the field, the greater the horizontal component at those stations over it, and hence the greater the value of the minor axis.

At each observation station we can plot a vector, being the ratio of the axes, and the direction of the plane of the ellipse; so that our map would show all the vectors pointing towards a good conductor, and reaching a maximum value above its boundaries. Joining points of equal vector magnitude, we get a contour system rising to peak values in closed curves surrounding good conductors, which will not only indicate the conductors, but also "outline" them on the ground surface.

Given satisfactory conditions, it is possible to estimate the depth of the conductor below ground surface, its dip, strike and area. Correct use of the method, and a proper appreciation of all the information obtained make this an extremely valuable and reliable method of investigation.

We cannot here give any further time to electrical methods; already I have discussed them more fully, relatively to the other methods, than should have been the case but for the fact that we employ them so successfully and are likely to develop them to an even greater extent in subsequent work.

THE SEISMIC METHOD.

This method is again totally different from those other three with which we have dealt in the sections—gravimetric, magnetic, and electric. It is a weapon of investigation which is invaluable for many conditions, and the only method which can be applied in some, particularly where investigations of formations at great depth (thousands of feet) are in question. For big scale work at depth (such as the investigation of "domes") the magnetic method may give positive results, when the actual observations are made with the greatest care and precision by a skilled and experienced observer, and correctly interpreted; the gravimetric method also may be of value there, some newer developments being applicable, particularly to formations on a tectonic scale, to considerable depths. But when one is reading very small departures from a normal value, and when those very departures may be less than the corrections which have been made, imagination is too likely to take control, even honestly, when a paid investigator is examining a field for a company which wants certain positive results. The seismic method, then, though entailing more expensive equipment, bigger field parties, and incidental operating expenses which are not necessary with the other two methods, gives definite results, enabling statements as to the nature, depth and distribution of the concealed formation to be made.

One seismic method—the reflection method—is now employed on most of our bigger modern ships. The problem there is to measure the distance below the ship through the water, to the lower, or solid formation, sea bed. A longitudinal progressive wave, which for the rest of this section we will call a " sound wave " (for such is its nature whether of audio frequency or not) is sent downwards until, reaching the bottom, some of the energy penetrates the medium as a sound wave therein, some is absorbed, and some is reflected back from the interface. This reflected wave reaches the apparatus at the ship, which records the time elapsing between the sending out of the signal and its return, and records automatically, in terms of this time and the known velocity of sound in sea water, the distance from ship to the land below. With some apparatus this is read only by eye, some device (such as a neon light at the appropriate depth on the scale) enabling the navigator to read and record the depth; with more modern apparatus the depth is actually recorded on a moving chemically treated paper, so that as the ship moves on its course and the paper unrolls, a contour picture is given, in hills and valleys, of the ocean bed. This is seismic prospecting. Unfortunately we cannot merely move forward with an apparatus over the land, graphing in such a manner the underground reflecting surfaces: the intervening material is irregular and far from homogeneous, there is great loss of energy by absorption, and we are often—generally—concerned with the three-dimensional problem, as though the ship were making its observations close to land, and getting back reflections from shore as well as sea bed.

Fessenden, the originator of the " depth finder " for ships, was also one of the first investigators of underground structure by seismic methods. We will not, however, consider his experiments, but merely the principles underlying modern methods.

The source of the sound waves in seismic prospecting is an explosion, from a few ounces to many tons of high explosive being employed.

The explosive may be buried properly in the ground (from a few feet to a hundred feet), so that little energy goes out in unwanted air waves, or it may merely be placed on the surface, depending on the size of the charges, where the work is being done, the cost of buying it, and who pays for the explosive. In our practice in Australia, we " jump " shot holes, fire a small charge in the bottom to " bull " a chamber there to take the larger charge, which is then packed down into the little cave thus formed, and the bore hole properly tamped. The shot is fired electrically, by dynamo-exploder and electric detonator. As we require the time elapsing between the sound wave setting out (when the explosion occurs) and the return of the echo to our detecting apparatus, a fine wire through the detonated plug of explosive is connected in series with leads to ground level—which may go back to headquarters to record electrically the instant of explosion (the break of the circuit) or which may be caused to broadcast a radio signal at that instant.

Explosive is expensive ; we do not confine ourselves to one detecting apparatus, but use a number of them (in Australia, up to six at a time have been employed) along a line traverse, so that sound waves which have gone down to reflecting and refracting layers will come back to a number of instruments ; the wave will also travel along the surface of the ground, and each instrument will detect and record the arrival of this wave also, as, in addition, it records the instant of explosion if a self-contained unit. (Here we have used a headquarters station connected with each detector : the recording equipment at headquarters marks the instant of explosion, and the instant of arrival of direct, reflected, and refracted waves at each of the six stations.)

In reflection seismic methods, the apparatus would record the instant of explosion, and the arrival at a detector of the direct ground wave, and of the reflected wave. By a number of instruments along a number of traverses in turn, the depth and slopes of bed rock could thus be examined. Many writers abroad are very enthusiastic about the reflection method ; but none of the curves I have seen show that it is very easy to pick up the record of arrival of reflected waves, as the apparatus is still generally disturbed by the waves, direct, which have arrived a very little earlier; the recording device is still agitated, and it is a question of experience in picking out the precise instant on the time graph of a change in the nature of the agitation.

We have preferred the refraction method, where the sound wave passes down through material in which it has a lower velocity than in the bedrock or formation sought. Entering this lower material the wave is refracted, and travels along with higher velocity; as this refracted wave progresses, the material at the interface is disturbed, so that waves with the lower velocity are continually being sent back to the surface. Detecting instruments near the explosion point will receive the direct surface wave first; those furthest away will receive the refracted wave first, because, although this wave has gone *down*, and *along*, and *up*, the " along " has been done so much quicker than the " along " through the upper medium that it more than compensates for the introduction of the relatively short time intervals for " down " and " up ". Then, drawing a graph in which abscissæ are distances from explosion point, and ordinates are time intervals between explosion and arrival of first transmitted disturbance at the appropriate detector, if there were no lower refracting layer in which the wave travelled with higher velocity the graph would be a straight line inclined at such an angle to the axes as would enable us to calculate only the velocity in the upper medium of transmission; if a lower refracting layer did exist, then this line would change its slope, the change in slope occurring at the distance from explosion point at which refracted wave and direct wave arrived together; after that point, refracted wave wins. By this refraction seismic method, employing a number of traverses, not only do we plot the depth and slope of the lower layer (or, as you may consider, layers if there are again lower ones of yet higher velocity of transmission), but we may also calculate the velocity of the sound wave through it, and thus, by a knowledge of materials and velocities, and a consideration of the geology of the district, give it a name.

There are many types of recording device; we have used here a six string Einthoven galvanometer, cross marking, by the interruption of the light past the strings on to the recording film or photographic paper, with lines at one hundredth of a second interval, so that we could estimate time intervals to one-thousandth of a second.

The "time of explosion" was electrically recorded, the break in circuit causing a kick in one of our Einthoven strings, which was also used to record the earth wave arrival at the most distant detecting microphone, the string having steadied in the meantime.

We had also one "Askania" seismometer, for experimental purposes. The detectors are also varied; we have used carbon granule types (several), moving coil types, and hot wire stethoscopic types. If reflection methods are employed, it is essential that the detector should steady immediately, so that the arrival of the later reflected wave may be observable accurately; if refraction methods are employed, this is not so important, as we are seeking instant of "first arrival".

If I were a wealthy company interested in prospecting for oil, I would not be content until I had at least one seismic section in the field. Its results are direct and definite; it is fully tested, millions of pounds sterling having been spent, with correspondingly great financial returns, on this one method abroad, particularly in the United States of America and in Persia; we are frightened of it here because it does mean training men, buying equipment, spending money to operate it and keep it in the field, and it cannot find oil formations unless those exist; and then cannot guarantee the oil. It is not a magic tool—but it is a tool; we would not attempt to print this address with an old hand press and loose type, yet we are content to waste money guessing rather than spend more and make sure by employing modern methods of prospecting.

IMPORTANT WORK BY GEOPHYSICAL METHODS IN AUSTRALIA.

A brief summary of work (divided under the sections set out in the main body of this address) which has been carried out in Australia will be of benefit to those who wish to know what has been done and where the results have been published.

The work of the Imperial Geophysical Survey is covered in the report to which reference has already been made,* so that undertakings subsequent to that date will be

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* "The Principles and Practice of Geophysical Prospecting." Cambridge University Press, 1931.

mentioned here. Naturally, all are not given, but sufficient to indicate the nature and diversity of the activity.

Gravimetric.

(1) A survey was carried out by the Department of Mines, N.S.W., at Corowa, to locate the position of alluvial-filled deep leads in this area of New South Wales, which were suspected to pass beneath the Murray River from Victoria, where they had been worked for highly profitable returns. The leads were located. Calculations showed their depth to be from 400 feet to 500 feet, which private enterprise has so far regarded as being too expensive to work. (Reference : Report, Department of Mines, N.S.W., 1933.)

(2) The Federal Government is assisting in the survey of the brown coal resources of Moorlands field, South Australia. The South Australian Government is interested in the possibility of establishing a central electrical power plant (on the lines of Yallourn, Victoria) and wishes to determine whether there are sufficient reserves there of brown coal. This survey is just commencing ; it presents much greater technical difficulties than did the survey of the I.G.E.S. at Gelliondale, Victoria.

(3) A gravimetric survey is proposed for a deep lead in Cape York Peninsula ; this work, which would be undertaken by the Geological and Geophysical Survey of North Australia, would investigate an auriferous lead overlain by recent sandstones.

Magnetic.

(1) A big area of the Gulgong district has been surveyed by the Department of Mines, N.S.W., to map the basalt-filled gold bearing deep leads of that district. The work was quite successful, several shafts having been sunk which corroborate the observations. So far no gold bearing wash has been obtained sufficiently rich to justify heavy expenditure in exploitation. (References : Annual Report, Department of Mines, N.S.W., 1930 ; *Mineral Resources*, No. 37, Mines Department, N.S.W.).

(2) A large scale survey, mainly to the east of this Gulgong field, has been made, in the vicinity of and above portion of the granite bathylith, to delimit the possible gold-bearing areas and thereby to outline the areas within which deep leads cannot be expected to carry gold bearing wash. (Reference : " A Magnetic Survey in the

Vicinity of a Granite Bathylith", This Journal, 1933 (1934), *67*, pp. 118-131.)

(3) A survey, requiring great precision of observation, was carried out for Oil Search Limited in Gippsland (Victoria) during a search for structural conditions suitable for the accumulation of oil. Actually, the problem was to locate irregularities in granite bed rock upon which structures of the buried ridge type may have been developed. (Reference: Publication by Oil Search Ltd., 1932.)

(4) A large scale survey of the Mittagong-Bowral district has been made, in an investigation of igneous intrusions, primarily to study the nature of the syenite mass "The Gib", thus shown to be an asymmetrical laccolith. (Reference: "A Detailed Magnetic Survey as an Aid to Geological Interpretation", This Journal, 1935 (1936), *69*, pp. 35-60.)

(5) A survey has been made of basalt-filled tin-bearing deep leads in the New England district (at Tingha, Emmaville and Stannum). This has been an economic success; following on the first of these the Mt. Topper tin mine was opened up at Tingha. Boring for test purposes is being undertaken at Emmaville and Stannum. (Reference: Annual Report, Department of Mines, N.S.W., 1932, *et seq.*)

(6) Work at Cobar, in progress and not yet published, is concerned with the search for gold-bearing leads, gangue minerals including pyrrhotite; conclusions have already been drawn concerning the possibility of mineralisation in the south-western portion of this important field. (Reference: Report, Department of Mines, N.S.W.)

(7) The investigations at the Darbalara dam site (Tumut River) were for a different purpose again; it was desired to determine the depth of rotten granite above solid granite, a matter of great importance in connection with the construction of the dam. Observations by the magnetic method gave a calculated depth of rotten granite as 40 feet; subsequent sinking of shafts proved an actual depth of 43 feet. (Not yet published, save in Departmental papers.)

Much work by this method has been done, and is to be done, by the "North Australia Survey" previously mentioned; the following references are to the work of that organisation. (For further details, see Annual Reports.)

(8) At Tennant Creek, Northern Territory, where gold is associated with ironstone bodies, a number of major anomalies have been discovered. So far four of these have been checked by drilling, and ore bodies have been found as predicted; the depths of the lenses beneath the surfaces range from 100 feet to 800 feet. The magnetic prospecting campaign has proved a marked technical success, and it now appears probable that a definite economic success also will be achieved. The results of the survey, predictions by which have been verified by drilling, throw much light on the nature of the ore occurrences, and show that there are potential ore bodies in the field at greater depth than had hitherto been suspected by the mining public, thus allowing a much more favourable view to be taken of the field. Following the survey, private enterprise in the field, on a large scale, has been stimulated. (Work carried out in 1935 and 1936.)

(9) A structural study has been made of certain features at Iron Range, Cape York. The country being covered by dense tropical vegetation, and there being a lack of outcrops and a considerable thickness of soil, geological interpretation of the underground structure has been assisted by a magnetic survey; some of the beds in a slate-schist series have been partly replaced by iron minerals, rendering this method practicable.

(10) Gold-bearing deep leads at Top Camp, North Queensland, have been traced by this method, as the wash contains large quantities (sometimes large boulders) of the magnetic material hæmatite.

Electric, Self Polarisation. (Natural earth potential methods.)

(1) The North Australia Survey has done a considerable amount of work by this method at Trekelano, Cloncurry district. A large number of indications having been obtained by the electromagnetic method, it was suspected that most might be due to highly conductive schists, and only a few to ore bodies; to determine which of the indications arose from oxidising sulphide bodies, the disclosed anomalies were examined more intensively by the self-polarisation method. Subsequent testing of two of these anomalies has revealed low grade copper-gold ore bodies beneath about 12 feet of alluvial cover. (Reference: Annual Report, N.A. Survey, 1935. More detailed reports are at present in press.)

(2) At Dobbyn, North Queensland, an investigation was made by the N.A. Survey, in 1935, of some copper-gold ore bodies. No boring tests there have so far been made.

(3) At Lolworth, Charters Towers district, Queensland, this method has disclosed anomalies which are to be tested by trenching. They are probably due to irregularly shaped ore bodies carrying gold and base metals in greisenised zones in granite, obscured by over-burden. (Reference: Annual Report, N.A. Survey, 1936.)

(4) Anomalies of great interest have been obtained at Dugald River, Northern Territory, where a search was carried out for bodies of lead sulphides; it is proposed to test these by shaft sinking shortly. (Reference: Annual Report, N.A. Survey, 1936.)

Resistivity Methods.

(1) This method was employed by the N.S.W. Department of Mines as a check on the observations made by the magnetic method; carried out in 1937, the results have not yet been published.

(2) A considerable number of investigations by this method have been made by the North Australia Survey as a check on the results obtained by other electrical methods; also with a view to testing ores, sediments, etc., for their conductivity, to determine the cause of anomalies disclosed by the other methods.

Equipotential Line Method.

Although this method is given in the main body of the address, as it illustrates the principles of other methods, it is no longer employed to any great extent anywhere throughout the world, so far as published records show. Fuller information can be obtained, for example, by the alternating current potential ratio method, referred to as "ratiometer" work.

A.C. Potential Ratio Methods: Ratiometer Work.

Investigations, other than by government surveys, have been carried out in Western Australia and in Victoria. The range of work by the government surveys has been considerable.

(1) Working for a private company, investigations were carried out by E. L. Blazey, M.Sc. (a member of the original I.G.E.S.) at Bethanga, Talgarno and Cassillis, in Victoria, over gold-bearing lodes. The results have not

been published; the technical side of the work appears in *Proc. A.I.M.M.*, No. 92, 1933.

(2) An important survey for the company was carried out at Mt. Lyell, Tasmania, by E. L. Blazey, which was an economic success, subsequent drilling and other mining operations proving the existence of the predicted new copper ore bodies.

(3) The Electrical Prospecting Company of Sweden made investigations at Cue, Western Australia, in the vicinity of the Triton mine, in 1933. This method was used in conjunction with an electromagnetic survey, and the results were generally satisfactory in determining the position of shear zones.

(4) The same company has also performed ratiometer surveys (accompanied by electromagnetic and self-polarisation observations) at Wiluna, Western Australia, on the northern extension of the main line of lode. Several shear zones were determined in 1933.

(5) A ratiometer survey (supported by electromagnetic observations) was made by this company in 1934 at Leonora, W.A., at the Sons of Gwalia mine. Testing of these results is in progress.

(6) The North Australia Survey, working at Silver Ridge, North Queensland, has demonstrated there that the mineralisation consists of a number of small isolated lenses of ore.

(7) This method was also adopted in searching for ore bodies in greisenised zones in granite, at Lolworth (Charters Towers district), North Queensland, by the N.A. Survey. The results have not yet been tested.

(8) In the Brock Creek district, Northern Territory, this survey carried out a search for auriferous quartz veins, under cover. Very extensive field work was done at Fountain Head, Yam Creek, Woolwonga and other places in the area, resulting in a number of reefs being discovered.

(9) The N.A. Survey, searching by this method in the Pine Creek district, Northern Territory, for quartz reefs under cover, has produced results which suggest that mining development here would be warranted.

(10) A similar survey, not yet complete, is being made in the Mt. Todd district, Northern Territory. (Most of these results, from the work of the North Australia Survey, will be found in their Annual Reports, or in work now in press.)

Electromagnetic Methods.

(1) In 1934, the Electrical Prospecting Company of Sweden employed electromagnetic methods at Allandale, Victoria, in tracing sub-basaltic deep leads. It is understood that the first results were disappointing, but that later results have proved satisfactory.

(2) The Swedish company, in 1936, using this method, prospected for a body beneath a cover of younger sandstones, at Mount Morgan, Queensland. Testing of these results is now in progress.

The next six pieces of work refer to the North Australia Survey, employing the electromagnetic methods.

(3) Structural studies at Mt. Freda (Soldier's Cap, North Queensland). Shear zones were traced here in 1935.

(4) In 1935 a very extensive survey was carried out at Trekeland, North Queensland. Subsequent testing showed small bodies of copper-gold ore.

(5) A structural survey at Dobbyn, North Queensland (1935), to locate copper-gold ore bodies, resulted in the tracing of a number of shear zones.

(6) Work during 1936 at Dugal River, North Queensland, enabled lenses of silver lead ore to be delineated ; this is shown to be a very promising area.

(7) A very large scale survey was made at Croydon, North Queensland, in 1936, auriferous quartz veins associated with graphite being traced under the sandstone cover.

(8) At Iron Blow, Brock Creek district, Northern Territory, the electromagnetic method has been employed for the examination of copper-gold ore bodies associated with shear zones. Mining developments are suggested.

This outline of work carried out in Australia from the closing of the Imperial Geophysical Survey in December, 1929, with a subsequent gap, is not supposed to be complete. Some work of a purely research nature, carried out either at a university or in the field, is omitted, and doubtless other work of a valuable nature has been omitted because it is not known to the author, or has been overlooked. I would be glad if readers knowing of such work, the results of which have been made available, would draw my attention to it.

GENERAL.

I have not attempted to make this address popular, in the bad sense, but have taken advantage of the fact that

I am addressing a body of scientists, and have employed scientific terms. I certainly have only surfaced the subject, so that I could give an outline of what is really an intensely interesting subject to a wider audience than the mere physicists who otherwise would read it.

I have endeavoured to avoid purely technical descriptions and discussions, and have not found it necessary to employ mathematics; you can get all that in appropriate articles prepared and published for those who require to know more about the subject. It is admittedly a difficult one; it does require the employment of considerable mathematical equipment; anyone cannot buy apparatus and go out and take readings; we have to be trained to interpret them.

This work is now a very definite and precise branch of geophysics; we could train the students here so that they would have a sound knowledge, theoretical and practical, of geophysical prospecting; we have students here who want to take up this work, we have companies who want to employ them. We have no chair of geophysics at any Australian university.

COMPOUNDS OF CREATININE WITH ALKALI HYDROXIDES.

By ADOLPH BOLLIGER, Ph.D.

(*Manuscript received, April 21, 1937. Read, June 2, 1937.*)

On adding a solution of creatinine in alcoholic sodium hydroxide to an alcoholic solution of picric acid, orange-red crystalline compounds are obtained, which are considered to be related to the compound which is the cause of Jaffe's colour reaction for creatinine. One of these compounds has already been examined and found to consist of one mol creatinine, one mol picric acid, and two mols sodium hydroxide. (Bolliger, THIS JOURNAL, 1936, *70*, 357.) In considering the structure of this compound, which has been called Compound I, one may assume the formation of a creatinine sodium hydroxide compound, because picric acid is able to accommodate only one sodium atom. Consequently an attempt was made to isolate these hitherto unknown alkali or alkali-hydroxide compounds of creatinine. The existence of a compound of creatinine with sodium hydroxide has already been indicated by the observation that creatinine dissolves more readily in alcoholic sodium hydroxide than in alcohol itself (Bolliger, THIS JOURNAL, 1936, *70*, 357). On further examination of this phenomenon with sodium, potassium, and rubidium hydroxide, it was found that approximately one and a half molecules of alcoholic alkali hydroxide are necessary to dissolve one molecule of creatinine, and, if one pours such a solution into ether, good yields of a crystalline compound are obtained.

EXPERIMENTAL.

A. Creatinine Sodium Hydroxide.

A half normal solution of alcoholic sodium hydroxide is prepared by dissolving pure sticks of sodium hydroxide in approximately 96 per cent. alcohol. Six to eight c.c. of this solution (3 to 4 millimol) and 0·226 grm. of creatinine (2 millimol) are transferred to a stoppered centrifuge tube and shaken. The creatinine present goes into solution.

Undissolved particles arising from impurities are centrifuged down and the clear solution is poured into another centrifuge tube containing about 30 c.c. of ether, which is also stoppered. Immediately a white crystalline precipitate forms, consisting of short fine needles. After standing for about half an hour, the mixture is centrifuged and the supernatant liquid is poured off. This fluid is alkaline in reaction, and on titration will be found to contain approximately the amount of sodium hydroxide added minus two millimols, which have combined with the two millimols of creatinine present, and which have been precipitated by the ether as a creatinine sodium hydroxide compound.

The precipitate is washed once with about 30 c.c. of a mixture consisting of six parts of ether and four parts of alcohol, then with ether. It is then dried *in vacuo* over calcium choride; yield 0·30 grm. The dried substance consists of small white needles which have a silky sheen. It does not melt, but begins to turn yellow at about 140° C., then it turns brown, and eventually black at about 190° C. It is hygroscopic and dissolves very readily in water. When added to alcohol, it is partly decomposed, as evidenced by the formation of a precipitate of creatinine. Aqueous solutions of this creatinine sodium hydroxide compound are strongly alkaline in reaction. By titrating it with 0·1 N or 0·01 N sulphuric acid while boiling, and using phenolphthalein as indicator, a sharp definite end point is obtained which can be verified by adding a known excess of acid to the hot solution followed by back-titration with standard alkali. Adding an acid indicator such as dimethyl-aminoazo-benzene or bromphenol blue to a fresh aqueous solution of this substance, then about twice the amount of acid is required to obtain a colour change of the indicator. The end point obtained with phenolphthalein as indicator represents the sodium hydroxide present in this compound as demonstrated by gravimetric determination of the sodium as sodium sulphate. The end point obtained with bromphenol blue represents the sum of the sodium hydroxide and creatinine present in this compound. This was proved by colorimetric determination by Folin's creatinine method (*Ztschrft. f. Physiol. Chem.*, 1904, *41*, 223), and by the dinitrobenzoic acid method (Bolliger, THIS JOURNAL, 1936, *69*, 224). According to these determinations, including nitrogen estimations (Table I), the compound consists of one molecule of creatinine, one molecule of sodium hydroxide, and one molecule of water,

TABLE I.

Analyses of Compounds of Creatinine with Alkali Hydroxides.

	Sodium.	Creatinine.	Nitrogen.
	%	%	%
A. Creatinine sodium hydroxide calculated for $(C_4H_7ON_3)(NaOH)H_2O$	13·4	66·1	24·5
Found	13·3	65·2	24·5
	Potassium.	Creatinine.	Nitrogen.
B. Creatinine potassium hydroxide calculated for $(C_4H_7OH_3)(KOH)2H_2O$	19·0	55·1	20·5
Found	18·9	54·6	20·4
	Rubidium.		
C. Creatinine rubidium hydroxide calculated for $(C_4H_7ON_3)(RbOH)2H_2O$	34·0		
Found	34·1		

or two molecules of water and one atom of sodium. On heating this compound *in vacuo* to 120° C., approximately two molecules of water are lost. The results obtained, however, are always somewhat low, viz. 20·5 per cent. of water instead of the theoretical value, 21·0 per cent. If the temperature is raised to remove the last trace of water, discoloration occurs. The dehydrated product, which must be some form of sodium creatinine, is fully hydrated again when treated with 90 per cent. alcohol. In this case the anhydrous sodium creatinine compound dissolves readily in the water containing alcohol, and if this solution is poured into ether the typical crystals of the original compound are obtained. Their identity was proven by titration with 0·01 N acid.

By using absolute alcohol for the preparation of the alcoholic sodium hydroxide solution, and pouring this solution into ether, a compound is obtained which, according to analysis, is a mixture of anhydride and monohydrate of creatinine hydroxide.

If one lets a solution of creatinine in alcoholic sodium hydroxide of about normal strength stand for several days, few but well formed crystals are obtained without adding ether. According to nitrogen analysis and titration with acid, these crystals also consist of one molecule of creatinine, one of sodium hydroxide, and one of water.

B. Creatinine Potassium Hydroxide.

This is prepared similarly to the sodium hydroxide compound. But, after pouring the solution of creatinine in alcoholic potassium hydroxide into ether, an oil is obtained. On standing in the refrigerator for several hours this oil solidifies, and above in the ether alcohol layer long white needles form. This compound is also very readily soluble in water, but considerably less so in absolute ethyl alcohol. The purified crystals melt in the capillary tube at 89° C., and according to analysis they represent a dihydrate of creatinine potassium hydroxide (Table I).

On heating this compound *in vacuo* at 150° C., 21·6 per cent. of its weight is lost in the form of water. This corresponds to a loss of $2\frac{1}{2}$ molecules of water (in theory 21·9 per cent.). The remaining half molecule of water cannot be removed by further heating.

C. Creatinine Rubidium Hydroxide.

This is prepared similarly to the sodium hydroxide compound. But, after pouring the solution of creatinine in alcoholic rubidium hydroxide into ether, an oil is obtained which crystallises on standing on ice. This compound melts approximately at 35° C. and may be an alcohol addition compound of the creatinine rubidium hydroxide compound. Its potassium content was found to be approximately 32 per cent. On heating it *in vacuo* at 60° C. it first melts and loses the alcohol, and then solidifies again. The crystals obtained now were found to contain 34·1 per cent. of rubidium, which would correspond to a creatinine rubidium hydroxide compound containing two molecules of water (Table I).

DISCUSSION.

It is difficult at this stage to assign definite structural formulæ to the compounds of creatinine with alkali hydroxides as described in the experimental part. On the preparative and analytical evidence presented, these compounds may be considered to be molecular compounds consisting of one molecule of creatinine, one molecule of alkali hydroxide, and one or two molecules of water. In support of this it may be mentioned that creatinine is known readily to form addition compounds with salts, such as zinc chloride, or with acids, such as hydrochloric acid. However, this is the first instance where molecular compounds with bases are described, creatinine demonstrating marked amphotheric properties. On the other hand the loss of two molecules of water on heating the "creatinine hydroxide compound" $(C_4H_7ON_3)(NaOH)H_2O$ (Table I) would indicate the existence of a sodium salt of creatinine with two molecules of water of hydration. For example, a keto-enolic change could be assumed, as suggested in a previous communication (THIS JOURNAL, 1936, *70*, 211), whereby the hydrogen of the enol group is replaced by sodium. But then again the formation by heating of a potassium creatinine compound retaining half a molecule of water also complicates this second hypothesis. But in any case these compounds will help to explain the colour reactions of creatinine with picric acid, dinitrobenzoic acid, trinitrobenzoic acid, and trinitrobenzol (Bolliger, THIS JOURNAL, 1936 *70*, 211), because, as will be shown in subsequent publications, alkali hydroxides of creatinine form the basis of the compounds responsible for these reactions. They are of further theoretical interest inasmuch as they may be considered as intermediates in the conversion of creatinine to creatine by means of alkali.

SUMMARY.

In an alcoholic medium creatinine forms with sodium, potassium and rubidium hydroxide, crystalline compounds which can be readily isolated and which consist of one molecule of creatinine, one of alkali hydroxide, and one or two of water.

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PRELIMINARY NOTE ON THE OCCURRENCE OF PALÆOZOIC STRATA NEAR TARALGA, N.S.W.

By G. F. K. Naylor, M.A., M.Sc.

(With Map and Sections.)

(*Manuscript received, May 21, 1937. Read, June 2, 1937.*)

Introductory.

In a previous paper published in this Journal,[1] the writer gave a general account of the geology to the north and east of Goulburn, giving evidence to show that, excluding the Permian, there were three main groups of Palæozoic rocks present, belonging respectively to the Ordovician, Silurian, and Devonian systems. In another paper,[2] published shortly afterwards, particular attention was devoted to the section from Goulburn to Bungonia, and an attempt was made to indicate the probable structure and relationships between the Palæozoic rocks.

It is the purpose of the present paper to record observations more recently made in the districts to the north and west of those previously dealt with, and to show how the Palæozoic formations in these regions may be correlated with those already described.

The areas under present consideration are indicated in the accompanying map. It must be emphasised that the geological boundaries sketched on it are only approximate, and are intended merely to indicate the general trend of the Palæozoic rocks. They do not take into account the presence of extensive flows of basalt, deposits of pisolitic bauxite (or laterite), and minor intrusions of various kinds of igneous rock, the extent of which has not yet been exactly determined. Their probable accuracy, however, may be gauged from the arguments adduced in the text and the numerous points shown on the map where detailed observations have been made and fossils collected.

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[1] "Note on the Geology of the Goulburn District, with special reference to Palæozoic Stratigraphy", This Journal, 1935, *69*, 75-85.

[2] "The Palæozoic Sediments near Bungonia: Their Field Relations and Graptolite Fauna", This Journal, 1935, *69*, 123-134.

It is not proposed here to discuss in detail the mutual relations of the Palæozoic rocks present, or to consider the precise nature of the folding to which they have been subjected, as this would anticipate the contents of a further paper, already in preparation, which has as its specific object such an interpretation of the regional structure.

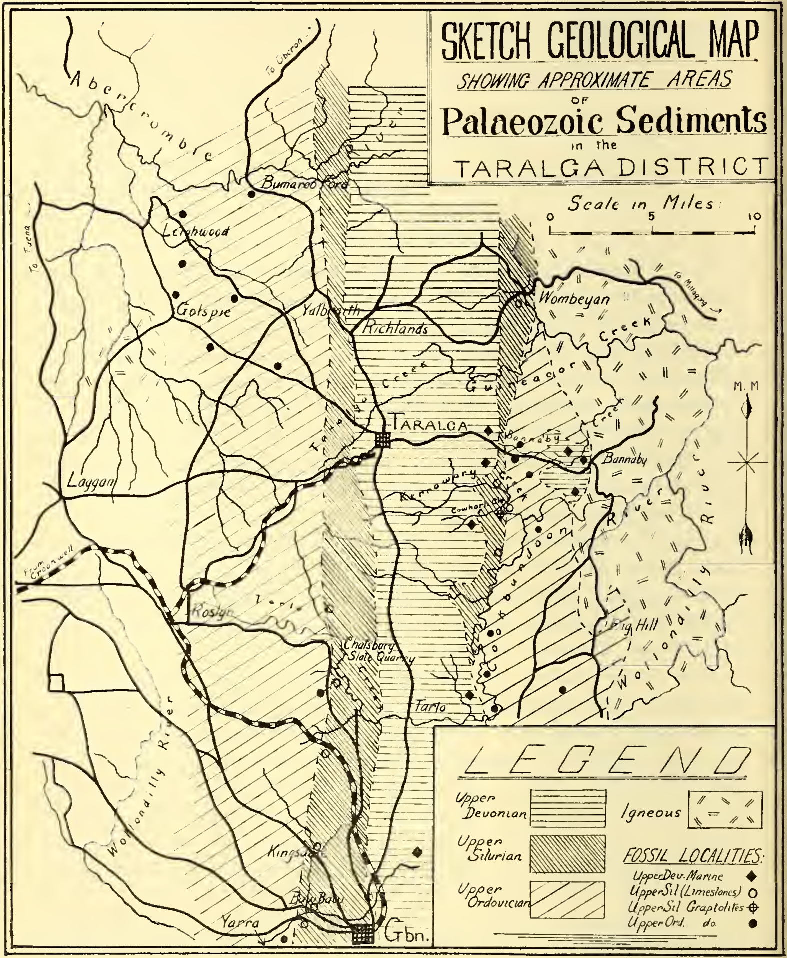

Fig. 1.

I. The Ordovician.

Two distinct belts of Ordovician rocks outcrop in the Taralga district, each trending meridionally and situated one to the east and one to the west of the town.

(*a*) The easterly belt is encountered on the Taralga-Bannaby road after descending Bannaby Hill in the direction of Bannaby. It consists mainly of slates interbedded with quartzites; in many places the slates are extremely silicified. This silicified slate has been used locally for road metal, and two small quarries at this point give good sections. The colour of the rock exposed in the quarries is the characteristic greyish-blue so frequently associated with the occurrence of graptolites in this district.

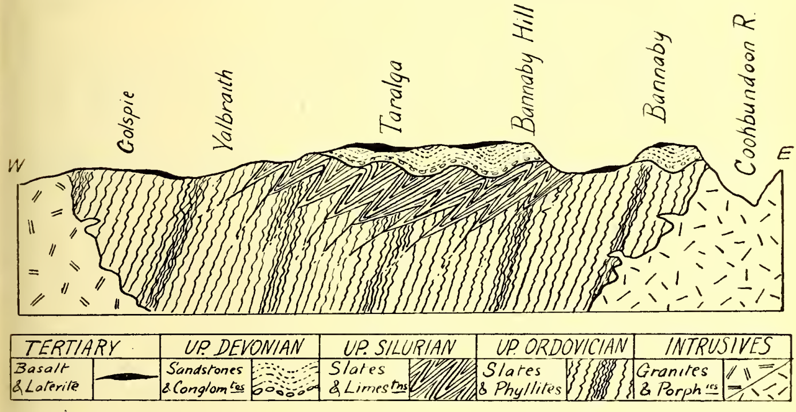

Fig. 2. Diagrammatic east-west section through Taralga, showing general relationship between the main geological units.

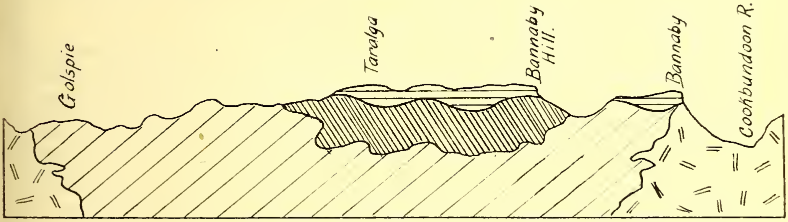

Fig. 3. Sketch geological section, not to scale, from Golspie to Bannaby, through Taralga. Shading corresponds to that on map.

Cross cleavage and extreme silification have rendered the fossils at this point rather obscure. However, generically recognisable specimens of *Diplograptus*, *Climacograptus*, *Dicellograptus* and *Dicranograptus* were obtained, pointing unquestionably to the Upper Ordovician age of the beds. A little further to the east, and about half a mile south of the road, the material is better preserved, and a good collection of Upper Ordovician forms was made at this spot.

Measured along the road, that is, approximately at right angles to the strike, the Ordovician belt appears to be about two and a half miles in width, being overlain on both sides by Upper Devonian strata. The predominant dip is westerly at high angles, and the folding is apparently isoclinal.

The belt runs north towards Guineacor Creek, but is largely concealed by Tertiary basalt, and appears to be interrupted by intrusive porphyritic rocks before reaching the vicinity of Wombeyan Caves. Southward it can be traced to Kerrawary Creek and the Cookbundoon River, and is undoubtedly continuous with the Upper Ordovician rocks found immediately to the east of the Cookbundoon Range in the vicinity of Towrang and Greenwich Park. Since these latter have been traced southwards beyond Windellama, the total length of the Ordovician exposure is not less than 50 miles, while the average breadth is about four or five miles.

(*b*) The westerly belt of Ordovician strata occupies a large area of country near the villages of Golspie and Yalbraith and the intervening districts. It extends north at least as far as Bumaroo Ford on the Abercrombie River. It can be traced southwards towards the Roslyn-Taralga railway line, where it is largely obscured by deposits of basalt and pisolitic bauxite (laterite) and is intruded by a gneissic granite. However, the hilly country between Roslyn and Chatsbury Slate Quarry is composed largely of slates lithologically similar to many of those of the Ordovician series, and about three miles south of the quarry the characteristic graptolite-bearing blue-grey slates are exposed on the roadside. It seems reasonable to assume that the outcrop continues southwards, passing to the west of Kingsdale and Baw Baw (where the limestones are known to be of Upper Silurian age), joining up with the Ordovician beds outcropping in the cutting of the Main Southern Line a little to the east of Yarra Station.

It would thus appear that the meridional extent of the westerly belt is in excess of 50 miles, with a width somewhat greater than that of the easterly belt.

The dips, as usual, are westerly, with every evidence of isoclinal folding. Lithologically both belts are similar, and contain the same graptolite fauna.

II. The Silurian.

As in the case of the Ordovician, Silurian rocks outcrop on both sides of Taralga, the trend in each case being also meridional.

Up to the present no very widespread outcrop of Silurian strata has been observed, and it seems possible that rocks of this age occur in rather restricted lenticular bands folded in amongst the Ordovician strata. On the other hand, what would otherwise be an extensive outcrop may be concealed by the overlying Upper Devonian strata.

(*a*) On the eastern side of Taralga on the banks of Kerrawary Creek occurs a massive outcrop of limestone, recorded by Carne and Jones.[3] This contains corals of a general Silurian type, and may tentatively be regarded as Upper Silurian. Possibly 200 feet in thickness, it has no great meridional extent, tapering out when traced in either direction.

About a mile further east is another outcrop of limestone not mentioned by Carne and Jones, situated at the junction of Kerrawary Creek and Cowhorn Gully. This is obviously a northerly continuation of a third outcrop which is recorded by Carne and Jones from the bank of the Cookbundoon River about a mile and a half upstream (i.e. south).[4]

Of the age of the limestone at the creek junctions there can be no doubt, for not only is it highly fossiliferous itself, but with it are interbedded black shales with a definite Upper Silurian graptolite fauna.

The limestone carries a wide range of marine fossils, these occurring most abundantly in impure, calcareous, shaly bands. A collection of specimens was submitted

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[3] " The Limestone Deposits of N.S.W. ", by J. E. Carne and L. J. Jones, Dept. of Mines, N.S.W., Min. Res. No. 25, 1919.

[4] This outcrop has not yet been examined by the writer on account of its inaccessibility.

by the writer to Dr. Ida Brown, to whom he is indebted for the following list of determinations :

Hercophyllum (*Cyathophyllum*) *shearsbyi* Sussmilch.
Favosites sp.
Strophomenid (*? Leptæna*).
Rhynchospira (*Retzia*) *salteri* Davidson.
Euomphalus cf. *centrifugalis* Chapman.
Murchisonia sp.
Small Pelecypod.
Encrinurus mitchelli Foerste.

The significance of the occurrence of graptolites in the interbedded shales is apparent when it is recognised that the forms occurring are of a very restricted range, and hence throw light on the precise horizon in the Silurian, at which the other marine forms occur. This knowledge should prove of value in other localities where fossiliferous limestones occur but graptolites are absent.

The two most prominent forms of graptolite occurring here are *Monograptus bohemicus* and *Monograptus chimæra*. These indicate that the zone present is that of *M. nilssoni*, i.e. the upper part of the Lower Ludlow stage. It will be noted that this zone is the same as that to which belong the Silurian graptolites from Towrang, and that the northern locality is in the line of strike of the southern one. The Upper Silurian belt may therefore be continuous from the latitude of Goulburn to that of Kerrawary Creek. There is no means of determining this, however, as its outcrop would be concealed by the Upper Devonian quartzites of the Cookbundoon Range. These latter have already been described as in unconformable contact with the Upper Silurian a little north of Towrang.

It is also interesting to note that the limestone at Wombeyan Caves is directly in the line of strike of this Silurian belt. In view of the short intervening distance, they may almost certainly be correlated with each other, and a Lower Ludlow age assigned to the Wombeyan outcrop. In this locality also there is little chance of determining whether the strata are entirely continuous on account of the easterly extent of the Upper Devonian rocks.

(*b*) On the western side of Taralga the nearest outcrop of rocks which may definitely be regarded as Silurian occurs on Tarlo Creek about a mile south of the Chatsbury Slate Quarries. Here there occurs a fairly large, though not conspicuous, deposit of highly fossiliferous limestone. The assemblage is typically Upper Silurian, and, though a full list of forms is not yet available for publication, an abundance of easily recognisable *Pentamerus knightii* leaves no doubt as to the Upper Silurian age of the outcrop.

Another outcrop of limestone is reported to occur about two miles upstream, i.e. about a mile above the quarry. The line joining these outcrops (and coinciding with the general strike of the southern one) passes to the west of the quarry, and hence would appear to place the Chatsbury slates themselves outside the limits of the Ordovician area. It has been generally believed that these slates are of Ordovician age, but reference to the original Mines Department report[5] shows that the Ordovician graptolites upon which this tentative conclusion was based were collected from loose boulders in the bed of the creek. It will be noted that before reaching the site of the quarry the Tarlo Creek runs east for some miles, traversing the Ordovician belt, so that the source of these graptolites can easily be explained, and they cannot be regarded as indicative of the age of the slates in the quarry. While there is no positive proof that these rocks are not Ordovician, three independent pieces of negative evidence point strongly to the conclusion that they are of Silurian age :

(*a*) They occur to the east of the line of limestones, and are hence outside the main Ordovician belt.

(*b*) The lithology is quite dissimilar to anything that has been met with in the known Ordovician regions.

(*c*) No trace of Ordovician graptolites has been found in the slates at the quarry. Mr. L. L. Waterhouse, who has examined these rocks intensively for economic purposes, agrees with the writer in this respect.

One small piece of positive evidence may be offered. At some time in the past an attempt was made to quarry slates in the valley of Sitwell's Creek near Towrang, the site of the quarry being within the Silurian zone in that district. Fragments of the slate, presumably from this quarry, were found and examined by the writer, and appear to correspond fairly closely with the purple variety at Chatsbury.

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[5] Annual Report, Dept. of Mines, N.S.W., 1913 (J. E. Carne and E. C. Andrews).

With regard to the general extent of the Silurian rocks to the west of Taralga, it should be noted that the limestones near Chatsbury are in line with those at Baw Baw and Kingsdale, and that limestone has been reported as occurring near the Forest Railway Station, i.e. about half-way between Kingsdale and Chatsbury. The Silurian outcrop at, and to the west of, Goulburn (previously recorded by the writer) may therefore be regarded as extending northwards at least as far as Chatsbury Quarry. So far there is no evidence of it much to the north of this, the outcrop, if any, being largely concealed by basalt, bauxite and tertiary sands.

III. The Devonian.

Rocks of Upper Devonian age occur extensively to the East of Taralga, where they occupy most of the high ground, though they are themselves largely concealed by basalt. They comprise the same series as that met with on the Cookbundoon Range further south. It should be remembered that the plateau at Taralga is about 800 feet higher than the Wollondilly Valley, and that the Cookbundoon Range seen from Taralga appears in the light of a southerly extension of this plateau rather than a range as such. Bannaby Hill, the highest point on the Taralga-Bannaby road, is in line with the main Cookbundoon Range, and like it is capped with quartzites. These contain the typical Lambian marine fauna, chiefly *Spirifer disjunctus* and *Rhynchonella pleurodon.* Neither here nor at any other part of the area can Devonian fossils be said to be abundant, but there is usually no difficulty in obtaining recognisable forms. At Bannaby Hill these occur on the roadside.

Similar fossils have also been collected from the quartzites occurring on the heights above Cowhorn Gully. In these localities the dip is similar to that of the eastern side of the Cookbundoon, that is, to the west, at varying low angles. Westward the dip flattens and the four or five miles between Bannaby Hill and Taralga appear to be occupied by Devonian quartzites and shales[6] amongst which red beds are conspicuous. This again is in accord with the state of affairs further south. A good outcrop of these red beds is met with in the valley of Taralga Creek where it crosses the Taralga-Richlands road. These beds appear to

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[6] Mostly concealed by Tertiary basalt.

correspond with those exposed near the village of Tarlo, and those which occur in the quarry at the southern end of the Memorial Hill at Goulburn.

From Richlands towards Wombeyan Caves the road passes for a long way over high ground on which quartzite outcrops lithologically identical with that of the Cookbundoon area. Though no fossils have yet been collected, the geographical position, altitude, and lithological characters would appear to justify one in regarding this as part of the main Upper Devonian series.

Another outcrop of Upper Devonian rocks occurs in the vicinity of the village of Bannaby Lithologically these are similar to those of the other regions, but easterly dips are frequent. Tuffaceous sandstones are included in small quantities, and also extensive conglomerates. Recognisably Upper Devonian brachiopods have been collected from the quartzites in numerous places.

This outcrop of Devonian strata appears to overlie Ordovician rocks to the west and to be in contact with igneous rocks (porphyrite) on the east and north-east. The northerly extent appears to be terminated by the valley of Guineacor Creek.

SUMMARY AND CONCLUSIONS.

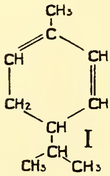
It is evident from the above that the general pattern of the Palæozoic rocks previously observed in the Goulburn district may be traced north practically as far as the Abercrombie River and Wombeyan Caves. Indications in these localities are such as to lead to the belief that subsequent investigation will show this pattern to extend even further. The area of the Devonian outcrop as shown on the latest edition of the State Geological Map must be considerably diminished, much of what has previously been regarded as a Devonian terrain being actually occupied by fossiliferous Upper Ordovician and Upper Silurian strata. Both Ordovician and Silurian strata occur in meridionally elongated belts, of which the Ordovician appear to be the more continuous, and both series have suffered isoclinal folding so that the dominant direction of dip is now towards the west.

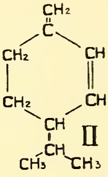
THE DETECTION AND ESTIMATION OF α-PHELLANDRENE IN ESSENTIAL OILS.

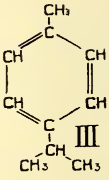
By Arthur John Birch, B.Sc.
(Communicated by Dr. F. Lions.)

(*Manuscript received, May 19, 1937. Read, June 2, 1937.*)

The well known nitrosite test for phellandrene (cf. Gildemeister and Hoffman, "Die Atherischen Öle", Vol, I, p. 432) is one of the most sensitive and reliable reactions in terpene chemistry. Easy to carry out, and sufficiently sensitive to give a recognisable precipitate with as little as 0·1 c.c. of α-phellandrene in 10 c.c. of p-cymene, it presents its only difficulty in the recrystallisation of the precipitated α-phellandrene nitrosite to constant melting point, particularly when only small amounts are available. It was probably this difficulty that delayed for so long the recognition of the existence of two separate phellandrenes—α-phellandrene (I) (△1 : 5 p-menthadiene) and β-phellandrene (△2 :1~~8~~ (7) p-menthadiene) (II).

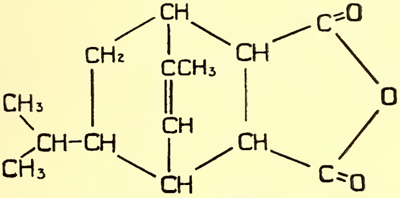

I


II


III

No reliable method for the quantitative estimation of α-phellandrene has so far been recorded. Isolation of a fraction of more or less correct boiling range, together with the nitrosite test for identity, constitutes the general procedure. Consideration of the variation in the physical constants recorded in the literature for various specimens of α-phellandrene from different sources clearly indicates that many of these are not pure. Indeed many of them probably contain relatively small percentages of α-phellandrene, which is readily detectable by the sensitive nitrosite reaction, in admixture with relatively large proportions of other less easily detectable substances. Thus, examination of a commercial α-phellandrene from eucalyptus oil (probably from *E. dives*) showed the presence of between 30% and 40% of p-cymene III, and it is probable that the occurrence of this hydrocarbon in varying percentages in the phellandrenes from the oils of a large number of eucalypts provides an adequate explanation of the wide variation in optical rotation recorded for them.

It is obvious that reliable methods for the detection with ease and certainty of α-phellandrene (I), especially in small amount, and for its accurate estimation in essential oils containing it, are greatly to be desired. In the present paper it is shown that suitable adaptations of the Diels-Alder reaction (*Ann. 460*, 98) can be made to furnish the desired methods. Diels and Alder (*loc. cit.*) have shown that admixture of benzene solutions of α-phellandrene and maleic anhydride, even in the cold, leads to the ready formation of a beautifully crystalline compound IV, melting at 126°-127° C.



IV

Addition also occurs with ease in ether, alcohol, or acetone solutions. Pure acetone is a particularly useful solvent, because of its volatility, its power of dissolving reactants and product, and its solubility in water.

If the terpene fraction of an oil containing α-phellandrene is mixed with a solution of maleic anhydride in acetone and the mixture allowed to stand for 30 minutes, and the unchanged oil and solvent removed by steam distillation, an oily residue is left which on cooling solidifies to a crystalline mass, which is obtained pure after one recrystallisation from alcohol. Excess maleic anhydride is hydrolysed during the steam distillation to water-soluble maleic acid. The addition compound IV is itself an acid anhydride, and might be expected to hydrolyse to some extent also. However, like the addition compound from maleic anhydride and cyclo hexadiene (Diels and Alder, *loc. cit.*), IV resists hydrolysis under the experimental conditions, and steam distillation for 15 minutes causes only about 5 per cent. of the anhydride to be hydrolysed to the corresponding acid. The slight volatility in steam of IV lowers the sensitivity of the method somewhat; nevertheless it has been found possible to detect with complete certainty as little as 0·05 c.c. of 1-α-phellandrene in admixture with 5 c.c. of p-cymene. It has also been found possible to detect small amounts of d-α-phellandrene in the terpene fraction of bitter fennel oil, the compound obtained having a m.p. of 126° C. It is doubtful if d-1-α-phellandrene could be detected so easily, as the inactive addition compound, formed by mixing equal weights of the active ones derived from d and 1 α-phellandrene, was found to be more difficult to crystallise, and to melt indefinitely at about 95° C.

This, however, affords a method of determining the rotation of a trace of α-phellandrene by means of a mixed melting point with a known sample of addition compound, and also of determining the presence of d-1-α-phellandrene in an optically active specimen.

It is obvious that the presence, even in small amount, of other conjugated dienes such as α-terpinene and β-phellandrene, must render the detection by this method more difficult.

Two methods have been evolved for the quantitative estimation of α-phellandrene. Accurate results cannot be obtained by collecting and weighing the compound IV obtained from a known amount of oil, since, as Lippman (*J.A.C.S.*, 1936, *58*, 1316) suggested, IV is not the only product of the reaction, and it is possible to obtain only about 75% of pure crystalline IV. It is therefore better to recover and measure the amount of oil left unchanged by the treatment with maleic anhydride, except where only very small amounts of α-phellandrene are present.

The first method depends on the fact that maleic anhydride and the addition compound, being acid anhydrides, both dissolve in hot caustic soda solution to give the sodium salts of the corresponding acids. The reaction is carried out in a Cassia flask and then excess of 10% caustic soda added, and the mixture heated on the water bath for 15 minutes. On cooling the volume of oil left is read off. This oil is pale yellow in colour, and contains no α-phellandrene (nitrosite test), and practically no high boiling material.

The second method involves the separation of the unchanged oil by steam distillation. The reaction is carried out in a distillation flask, and, after the solvent has been removed, excess alkali is added to facilitate the removal of the volatile portion of the oil, and the mixture steam distilled. The volume of the oil which has come over is then read off.

Determinations by these two methods carried out on known mixtures of α-phellandrene and p-cymene, cineol, α-pinene and limonene, agreed quite well, results by the first method being usually a little lower than those obtained by the second.

These methods cannot be used when other substances are present which react with maleic anhydride, so that oils containing many oxygenated compounds, especially alcohols, or α-terpinene or β-phellandrene, cannot be used.

Apart from their value as methods of estimation, these processes have the advantage that the rest of the oil is recovered unchanged, and can be examined for other constituents.

Treatment with maleic anhydride could thus be made a standard procedure in the examination of all oils containing conjugated dienes.

EXPERIMENTAL.

Detection.

In a typical experiment 1-α-phellandrene (0·1 c.c.), p-cymene (10 c.c.), acetone (10 c.c.) and maleic anhydride (0·2 grm.) were mixed in a 100 c.c. distilling flask having a neck 12 cm. long between the bulb and side arm. The neck should not be any shorter, as there is danger that the material may splash over during the subsequent steam distillation. After standing for an hour the solvent was distilled off on the water bath, and then steam blown through the mixture until oil ceased to come over. The residual oil solidified on cooling, and was recrystallised from alcohol (0·5 c.c.); m.p. 126° C.

Estimation.

First Method. The α-phellandrene mixture (8 c.c.) was mixed with acetone (10 c.c.) and maleic anhydride (6 grm.) in a 100 c.c. Cassia flask, and the mixture left to stand for an hour. The acetone was then boiled off on the water bath, and 10% caustic soda solution (40 c.c.) added. The flask was heated on the water bath with frequent shaking for 15 minutes, by which time all the alkali-soluble material had been removed. The mixture was cooled, and filled to the stem with 10% caustic soda solution and the volume read off. Water should not be used to fill the flask, as emulsification usually occurs.

The α-phellandrene fraction used was shown to contain about 35% p-cymene. It had the physical constants

N_D (16°) 1·4780
α_D (15°) —65°.

50 c.c. of the fraction gave in successive determinations 17 c.c. and 18 c.c. of residual oil. This oil had the constants

N_D (15°) 1·4900
α_D (15°) +0·13

and gave p-hydroxyisopropyl benzoic acid (m.p. 156°-157°) and terephthalic acid on oxidation, proving it to be p-cymene.

The estimations were carried out on a mixture of α-phellandrene fraction (4 c.c.) with other terpenes (4 c.c.), the results being expressed as the percentage of α-phellandrene in the original fraction. These results are comparatively constant, thus proving the applicability of the method.

Diluent.	Results.		
p-cymene	Residual oil	5·4 c.c.	5·3 c.c.
	α-phellandrene	2·6 c.c.	2·7 c.c.
	Percentage in original fraction	65	67·5
cineol	Residual oil	5·4 c.c.	
	α-phellandrene	2·6 c.c.	
	Percentage in original fraction	65	
limonene	Residual oil	5·2 c.c.	
	α-phellandrene	2·8 c.c.	
	Percentage in original fraction	70	
α-pinene	Residual oil	5·4 c.c.	
	α-phellandrene	2·6 c.c.	
	Percentage in original fraction	65	

Second Method. The reaction was carried out as before, this time in a long necked distilling flask (100 c.c.). After the acetone had been distilled off, 10% caustic soda solution (40 c.c.) was added and steam blown through the mixture. The distillate was received in a Cassia flask, and when oil had ceased to come over the flask was filled to the neck and the volume of oil read off.

50 c.c. of the α-phellandrene fraction gave 15 c.c. of p-cymene, or 70% α-phellandrene.

Diluent.	Results.	
p-cymene	Residual oil	5·3 c.c.
	α-phellandrene	2·7 c.c.
	Percentage in original fraction ..	67·5
cineol	Residual oil	5·3 c.c.
	α-phellandrene	2·7 c.c.
	Percentage in original fraction ..	67·5

The results obtained by the two methods are thus seen to be concordant.

Stability of IV to Boiling Water.

The addition compound IV (2 grm.) was placed in a 100 c.c. flask and submitted to steam distillation for 15 minutes. The cooled residue was then added to water, and titrated with N NaOH, using phenolphthalein as the indicator; 0·5 c.c. of alkali was required, showing only about 5% conversion of the anhydride to the acid. The distillate (150 c.c.) contained 0·05 grm. of IV.

ACKNOWLEDGMENTS.

The author wishes to express his thanks to the Commonwealth Government for a Research Scholarship, to Messrs. Thomas and Cameron, of Mortlake, for a gift of *E. dives* oil, and to Dr. F. Lions for his interest in this work.

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RED COMPOUNDS FORMED BY PICRIC ACID AND CREATININE IN THE PRESENCE OF SODIUM HYDROXIDE.

By ADOLPH BOLLIGER, Ph.D.*

(*Manuscript received, June 24, 1937. Read, July 7, 1937.*)

In a previous communication (THIS JOURNAL, 1936, *70*, 357) an orange-red crystalline compound was described which was obtained by adding two molecules of picric acid to a solution of one mol of creatinine in about two and a half mol of alcoholic sodium hydroxide. Under somewhat changed experimental conditions, such as the addition of an increased amount of sodium hydroxide, different compounds were obtained which were characterized by a smaller picric acid content. Shortly afterwards, however, it was observed that creatinine forms with alkali hydroxides crystalline compounds which were considered to be intermediate in the formation of these red compounds (THIS JOURNAL, 1937, *71*, 40-44). Since these alkali hydroxide compounds, and particularly the sodium hydroxide compound, are easily isolated, it was decided to study the formation and nature of these red compounds by adding to equimolecular mixtures of "creatinine sodium hydroxide" and picric acid varying amounts of sodium hydroxide.

EXPERIMENTAL.

In a centrifuge tube one millimol (0·171 gm.) of creatinine sodium hydroxide monohydrate was dissolved in about 0·8 c.c. of water. To the aqueous solution was added one millimol of picric acid (0·229 gm.) dissolved in about 20 c.c. of absolute alcohol. From this yellow mixture a trace of a reddish compound precipitated, which was removed by centrifugation. On adding about an equal amount of ether to this mixture 0·9 gm. of a precipitate

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* Acknowledgments are due to Miss Dorothy Dark for valuable technical assistance.

was obtained consisting mostly of creatinine. After adding more ether, crystals of sodium picrate were obtained. But on adding alcoholic sodium hydroxide to a clear mixture of creatinine sodium hydroxide and picric acid, the formation of a fairly large red precipitate was observed. The yield increased with increasing amounts of sodium hydroxide added. It reached an approximate maximum, i.e. 0·4 gm., after the addition of one millimol of sodium hydroxide. The mixture, after standing for two hours, was centrifuged and the supernatant fluid was decanted. This fluid was alkaline in reaction but contained only about 5 per cent. of the sodium hydroxide originally added.

The red precipitate was washed once with a mixture of three parts of alcohol and seven parts of ether and then with ether. After being dried *in vacuo* the precipitate was a bright red crystalline powder, which, on heating, darkened but did not melt. This compound was very soluble in water, forming a deep red solution but little soluble in alcohol, forming a yellow solution. On evaporation of the concentrated solution at room temperature large red needles were obtained. But on heating such a concentrated solution decomposition took place, and on cooling crystals of sodium picrate appeared. Solutions of this compound were alkaline in reaction, and on titration with phenolphthalein as indicator they were found to contain approximately one "free" atom of sodium. However, an analysis of the red crystals for sodium, picric acid, and nitrogen, indicated a compound consisting of two molecules of sodium hydroxide, one of picric acid, one of creatinine, and two of water (Table A, Experiment 1). The two molecules of water could be removed by heating the compound in moderate vacuum at 120° C. The resulting anhydride in all respects was found to be identical with the red compound $(C_4H_7ON_3–C_6H_3O_7N_3)$ (2NaOH) described in a previous paper as Compound I (THIS JOURNAL, 1936, *70*, 357). On adding mineral acid it also formed a red isomer of creatinine picrate.

Subsequently 1½, 2, 2½, 3, 3½, 4, 6, and 8 millimols of sodium hydroxide were added to solutions containing 1 millimol of creatinine hydroxide and 1 millimol of picric acid. In every instance a red or orange precipitate formed immediately after the addition of the alkali. It was centrifuged down, freed from the supernatant fluid and washed first with alcohol and then with an alcohol ether mixture till the alkalinity of the wash fluid became

TABLE A.—*Composition of precipitates obtained after the addition of varying amounts of alcoholic sodium hydroxide to a mixture consisting of one millimol of creatinine hydroxide and one millimol of picric acid.*

Experiment Number.	Sodium Hydroxide Added.	Sodium Hydroxide Recovered.	Resulting Precipitate Found.		Calculated.		Theory.
			Picric Acid.	Sodium.	Picric Acid.	Sodium.	
1	Millimols. 1·0	Millimols. 0·05	% 50·2	% 10·0	% 50·0	% 10·0	Compound I Dihydrate $[(C_4H_7ON_3–C_6H_3O_7N_3)\ (2NaOH)]\ 2H_2O$
2	1·5	0·11	47·0	10·9			
3	2·0	0·62	48·1	12·1	47·9	12·0	Compound II Tetrahydrate $\{[(C_4H_7ON_3–C_6H_3O_7N_3)\ (2NaOH)]_2\ (NaOH)\}\ 4H_2O$
4	2·5	0·68	46·2	13·4	46·0	13·8	Compound III Dihydrate $[(C_4H_7ON_3–C_6H_3O_7N_3)(3NaOH)]\ 2H_2O$
5	3·0	0·95	45·4	14·2			
6	3·5	1·42	44·3	13·7			
7	4·0	1·53	43·8	15·3	44·2	15·5	Compound IV Tetrahydrate $\{[(C_4H_7ON_3–C_6H_3O_7N_3)\ (3NaOH)]_2\ (NaOH)\}\ 4H_2O$
8	6·0	3·42	44·4	15·8			
9	8·0	5·33	42·9	15·9			

negligible. Ultimately the precipitate was washed with ether and dried *in vacuo.* In each experiment the supernatant fluid and the wash fluid were then combined and titrated with 0·1 N sulphuric acid using phenolphthalein as indicator. As shown in Table A, the sodium hydroxide thus recovered in experiments 3 and 4 is roughly half a millimol. This would indicate that of the two millimols added in experiment 3 (Table A) one and a half have been utilized by the red precipitate formed. In experiment 4 two millimols of alkali have been used up from the two and a half added. Also in experiments 5 and 6, after the addition of three and three and a half millimols of sodium hydroxide respectively, two of alkali have been taken up, judging from the alkali recovered in the supernatant fluid. In experiments 7, 8, and 9, three and a half millimols have been used up according to the alkali recovered in supernatant fluids and wash fluids.

The dried precipitates were bright red except in experiments 8 and 9, where they were found to be orange-red. They were all found to dissolve very readily in water with a deep red colour. However, in the course of a few days the colour faded to yellow in experiments 1 and 2. It was more stationary in the following experiments, and especially in experiments 7, 8, and 9. The precipitates were analysed for picric acid and sodium content. According to the analytical findings and according to the amount of sodium hydroxide taken up in the process of their formation, they were classified as Compounds II, III, and IV. Their proposed provisional formulæ are listed in Table A.

In another series of experiments the sodium hydroxide compound of creatinine was not isolated. Creatinine was simply dissolved in a known amount of alcoholic sodium hydroxide. For example, one millimol of creatinine was dissolved in 6 c.c. of alcohol containing 2·8 millimols of sodium hydroxide. One millimol of picric acid was dissolved in about 20 c.c. of 95 per cent. alcohol. After mixing the two solutions a red precipitate was obtained, the yield being 0·39 gm. According to picric acid and sodium determinations the precipitate corresponds to Compound II (Tables A and B). Using absolute alcohol instead of 95 per cent. alcohol the anhydride form of Compound II was obtained as shown by analysis (Table B). On heating this compound at 80° C. in high vacuum two more molecules of water were given off (Table B). By using four millimols of sodium hydroxide and 95 per cent.

TABLE B.—*Composition of precipitates obtained after the addition of one mol of creatinine dissolved in alcoholic sodium hydroxide to one mol of picric acid dissolved in alcohol.*

	Picric Acid. %	Creatinine. %	Carbon. %	Hydrogen. %	Nitrogen. %	Sodium. %
Dihydrate of Compound II prepared with 95% alcohol:						
Calculated	47·9					12·0
Found	47·5					11·8
Compound II prepared with absolute alcohol:						
Calculated	51·7	25·5	27·1		19·0	13·0
Found	50·8	24·7	26·7		18·7	12·8
Compound II after high vacuum treatment:						
Calculated			29·4	2·8	20·6	14·1
Found			29·7	3·6	20·5	13·9
Dihydrate of Compound III:						
Calculated	46·0					13·8
Found	45·2					13·3

alcohol a precipitate was obtained corresponding to Compound III.

Finally, it should be mentioned that the dihydrate of Compound I was obtained by mixing solutions of equimolecular amounts of sodium picrate and creatinine hydroxide. The sodium picrate was dissolved in alcohol and the creatinine hydroxide was dissolved in water.

All these creatinine picrate sodium hydroxide compounds were treated with mineral acids, and in all instances the "red isomer" of creatinine picrate was obtained, as shown by picric acid determinations. The best yields were obtained as follows: 2 c.c. of 2 N hydrochloric acid in a centrifuge tube are cooled to approximately 0° C. 0·1 gm. of the creatinine picrate sodium hydroxide compound, for example Compound II, was added in small amounts. A bright red crystalline precipitate formed, and the mixture, while still cold, was rapidly centrifuged. After decanting the supernatant fluid the precipitate was washed three times with about 0·5 c.c. of water, then it was dried, washed several times with benzol, and dried again. The picric acid content of the red isomers originating from the different sodium hydroxide compounds of creatinine picrate varied from 65 to 67 per cent. (theory, 67 per cent.).

Discussion.

The essential reaction that takes place when mixing equimolecular solutions of creatinine sodium hydroxide and picric acid seems to be the formation of yellow sodium picrate and colourless creatinine. As soon as additional sodium hydroxide is added the mixture turns red and a red compound is formed which increases in yield until an equimolecular amount of alkali is present. As shown by analyses, the resulting red crystalline precipitate is a pure compound, the dihydrate of Compound I (Table A). Compound I was obtained before under essentially similar experimental conditions, in which case the excess of picric acid added (two mols for each mol of creatinine) was neutralised by a corresponding excess of sodium hydroxide (This Journal, 1936, *70*, 357).

If more sodium hydroxide is added, Compound I is able to take up more alkali. However, the addition of one and a half mol to the creatinine hydroxide picric acid mixture did not seem to furnish a clear-cut compound as shown in experiment 2 (Table A). But by adding two molecules a precipitate is obtained consisting of two molecules of Compound I and one molecule of sodium hydroxide. Much preparative and analytical evidence proves the existence of such a molecule (Compound II). By adding from two and a half to three and a half mols of sodium hydroxide a precipitate formed which consists of one molecule of creatinine picrate, three molecules of sodium hydroxide, and two of water (Compound III). The limit of saturation with alkali, however, is reached in Compound IV, which consists of two molecules of Compound III plus one molecule of sodium hydroxide. The same molecule formed after the addition of 4, 6, and 8 mols of sodium hydroxide (Compound IV).

As shown by their preparation, composition, and ready conversion into the red form of creatinine picrate, the four compounds described are very closely related to each other. But at this stage no attempt will be made to elucidate further the structure of these compounds. This will be done on another occasion in connection with the examination of the nature of the red isomer of creatinine picrate and similar compounds.

The present investigation has been undertaken to explain the mechanism of Jaffe's reaction for creatinine. Earlier researches in this field were mentioned in a previous paper (This Journal, 1936, *70*, 357). Greenwald, in his latest paper on this subject (*Journ. Biol. Chem.*, 1928, *80*, 103), prepared a compound whose composition he claimed to be one molecule of creatinine picrate and two molecules of sodium hydroxide. This compound he considered to be the cause of Jaffe's reaction. It was obtained by adding alcohol to a mixture of about one mol of creatinine, two and a half of picric acid, and three molecules of sodium hydroxide dissolved in a small amount of water. However, the yield was only 25 per cent. and the analyses given for this compound were not convincing. For these reasons the problem could not be considered to be solved. In addition to the unsatisfactory analyses, which were probably due to the non-homogeneous nature of the precipitate, it must be kept in mind that the preparation of Greenwald's substance depends on the addition of an insufficient amount of sodium hydroxide when compared with Jaffe's reaction, where about eight to ten molecules of sodium hydroxide are added for every molecule of picric acid. In order to obtain a colour that is deep enough to compare with Jaffe's reaction for a similar amount of creatinine, more sodium hydroxide and some picric acid has to be added to Greenwald's compound when dissolved in water. A similar objection can be raised against Compound I, which on a previous occasion was considered to be a probable cause of Jaffe's reaction (This Journal, 1936, *70*, 357). But, after examining the nature of Jaffe's colour reaction, one is forced to the conclusion that Compound IV is the most likely compound underlying the colour test for creatinine with a strongly alkaline picric acid solution. Compound IV represents the limit of saturation with sodium hydroxide possible with the red form of creatinine picrate. The colour of its aqueous solution is of sufficient intensity to compare with that obtained by a similar amount of creatinine in Jaffe's colour reaction. Furthermore, the stability of its aqueous solution closely resembles that of a solution under the conditions of Jaffe's test.

SUMMARY.

The red compounds formed in an alcoholic medium by picric acid and creatinine in the presence of varying amounts of sodium hydroxide have been studied. Four compounds have been isolated. They are characterized by a varying sodium or sodium hydroxide content. Compound I consists of one molecule of creatinine, one of picric acid, and two of sodium hydroxide. Compounds II, III, and IV contain two and a half, three, and three and a half molecules of sodium hydroxide for each molecule of creatinine. Compound IV represents the maximum degree of saturation and has been considered as the most likely cause of Jaffe's reaction.

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SOME PROBLEMS OF THE GREAT BARRIER REEF.*

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INTRODUCTION.

The honour bestowed by your invitation to deliver the Clarke Memorial Lecture is deeply appreciated, not only on account of the distinction involved, but also because I have always been a great admirer of the eminent pioneer geologist, W. B. Clarke, who was the first to carry out geological work in an area—that of Silverwood, near Warwick, Queensland—which some years ago concerned me greatly from a geological point of view.

In casting around for a subject on which to address you this evening it has been deemed fit to discuss some of the problems associated with a region which has engaged my attention closely for the last 14 or 15 years—the Great Barrier Reef. It is not reasonably possible to deal exhaustively with this matter except in a somewhat lengthy course of addresses, and anything like a complete dissertation on the area, if carried through at all thoroughly, would be unduly long and possibly not really worth while in view of the incomplete nature of our existing knowledge of the area.

Following upon a visit to the first Pan-Pacific Science Congress in Honolulu in 1920, it became apparent that in Australia we were not playing as full a part as we should in the elucidation of the problems of the Pacific.

Steps were taken, therefore, to form something in the nature of a Research Committee, which might supervise and conduct investigations so as to afford the scientific world an adequate account of the nature and origin of what, after all, is the greatest mass of coral the world has ever known. This committee, called the Great Barrier Reef Committee, and which is centred in Queensland, is

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* Clarke Memorial Lecture delivered to the Royal Society of New South Wales, April 19, 1937.

composed of representative scientific investigators in all the Australian States, New Zealand, and Great Britain.

Private individuals, public institutions and governments—British, Commonwealth and State—have lent their patronage, backed with hard cash, and some of us have worked year in and year out on the long and interesting task of answering some of the many riddles associated with a study of this great coralline mass. You will be interested perhaps in hearing what some of these problems are and of the progress we have made in offering adequate explanations.

HISTORICAL.

Before doing this, however, it is essential that you know a little of the history of the area.

James Beete Jukes, the naturalist on H.M.S. *Fly*, which during the early part of 1843 was surveying in the Barrier Reef waters, commenced his narrative of the "Voyage of H.M.S. *Fly*", published in 1847, thus: "On January 7, 1843, I landed for the first time in my life on a coral island. This was a little islet called the First Bunker's Island, in the northern part of the Capricorn Group . . ." In this narrative he gives, I believe for the first time, a description of the Great Barrier Reef, and by means of a diagram he indicated definitely his belief in a stupendous thickness of the coralline deposit and also in Charles Darwin's conception of the origin of coral reefs.

Some 73 years earlier, in 1770, James Cook had made an accidental acquaintance and one rather more intimate that he cared for, of the maze of coral reefs as he sailed north from Botany Bay. He really knew little of the coralline mass as his interest unquestionably was that of the terrigenous islands and coastline. However, on June 1, 1770, he found his ship, H.M.S. *Endeavour*, firmly fixed on a coral reef which he named the Endeavour Reef. After much jettisoning of cannon and other gear he got off, fothered the vessel, using a sail with oakum, etc., to fill the hole, and made his way a few miles in a N.W. direction by the help of the S.E. trades till he found the river which he named the Endeavour River. Here, on the site of what is now Cooktown, he repaired his good ship and set sail northerly along the coast. After travelling some distance north and finding the reefs becoming more abundant, along with his mate he climbed the granitic island—Lizard Island—some 1,000 feet above sea-level and gazed out over what to him appeared to be a cruel maze of coral reefs. He saw for the first time the dangers through which he had been navigating and he decided to seek safer, if somewhat rougher, waters. To that end he took a bearing on one of the openings through the Outer Barrier with its deep channel leading towards the deep blue ocean of prodigious depths outside the reef mass. Out he sailed and thanked his Maker for his deliverance from these treacherous coral reefs. He set off on a northerly course parallel to the Outer Barrier, and, try as he would, because of wind and tide he had to fight with all his might to fend his vessel off the cruel and jagged coral growths along the Outer Barrier.

Eventually, when abreast of what is now Cape Weymouth, Lat. 12° 37′ S., the wind and tide took control and wafted him inside the Outer Barrier again through a passage somewhat similar to the one he used for the purpose of getting out previously. He was more than pleased to find himself inside again, safe and sound, and so he called the passage Providential Channel. It is worthy of note that some ten miles south, east of Cape Direction, Bligh, Cook's one-time lieutenant, came through a passage in the Outer Barrier ten years later in his wonderful voyage in a life-boat after the mutiny on H.M.S. *Bounty*. Some 60 to 70 miles further north is yet another entrance in which H.M.S. *Pandora*, under the command of Captain Edwards, was wrecked in 1791 on her way back from the Society Islands with such of the mutineers as could be captured.

The northern part of this Great Barrier Reef is rich in association with historical happenings of great interest, but it is not so much of these things that we wish to speak this evening, but rather of more scientific aspects of this extraordinary region.

Extent and General Features of the Great Barrier Reef.

Jukes clearly indicated the lack of continuity of the line of reefs making up the Outer Barrier and spoke of them as "reeferies".

The Great Barrier Reef extends for some 1,200 miles, from near the mouth of the Fly River in Papua down almost to Breaksea Spit at the northern end of Fraser or Great Sandy Island to the east of Bundaberg.

In its northern half it is much more continuous, more compact, and more of an entity than in its southern half. Moreover, it is much nearer to the coastline north of Cairns than to the south. Near Cape Melville (Lat. 14° 10′ S.) it is only some 10–12 miles from the land. Southward from Cairns the Outer Barrier line begins to diverge from the coastline and the reefs become less definite until towards its southerly end it is a matter of some 200 miles from the coastline to the edge of the coral mass.

Professor J. Stanley Gardiner and others such as Michael Spender* have emphasised this difference between the northern and southern portions, and the former definitely believes that, while the coral reefs in the northern end may be flourishing and the mass as a whole more than holding its own, the same cannot be said of the southern end. While one sees some justification for this view, it is largely a matter of opinion. First of all, we have no past record with which to compare the existing development, and, secondly, very few people have ever seen or traversed to any extent the reefs at the outer portions on the southern end; the few who have do not appear to have been scientific investigators. If indefiniteness of form and lack of continuity of the outer barrier line mean a less flourishing coralline mass the opinion may be accepted.

It must be appreciated, however, that in the Bunker and Capricorn groups of coral islands many very flourishing coral reef patches exist today. Dr. C. M. Yonge, after his studies for approximately one year in the central and northern portions of the Barrier Reef, visited these southern coral cays, and he was surprised at the flourishing condition of the coral reefs.[1] Other scientific investigators have been impressed similarly. The wealth of variety characteristic of the northern end is not to be seen here, but there is much virility in the growth even if it is less highly coloured.

Before accepting the opinion as to decadence, some quantitative work would need to be carried out. Maybe the proposed deep boring operations at Heron Island will shed some light on this question.

Before leaving this point it should be mentioned that in Moreton Bay at Peel Island (Lat. 27° 30′ S.) there are several quite large coral reefs with really luxuriant coral

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* *Geogr. Jour.*, 1930, p. 275.

[1] C. M. Yonge, "A Year on the Barrier Reef", p. 202.

growths, and near the mouth of the Brisbane River, on Mud Island, fine growths especially of *Turbinaria* may be seen. In the past at Mud Island the coral growth unquestionably has been much greater than today, but even in the north, at Thursday Island, the sites of once luxuriant coral patches are now a mass of dead coral.

Attempts by the late Charles Hedley and the author to find, for the purpose of remeasuring, several flourishing reefs photographed and measured with great accuracy by Saville Kent, proved abortive ; not because of the difficulty of fixing the location, but because of the subsequent destruction. The coral reefs off Vivian Point at Thursday Island (Lat. 10° 30′) and on Stone Island (Lat. 20° S.) in Bowen Harbour, are the two most easily checked illustrations of this contention.

One is forced to accept the view that there is no permanency about the flourishing conditions of coral reef patches in relatively shallow water patches. What degree of permanency there may be in the deeper waters of the lagoon area of the Great Barrier Reef is another question.

The factors of temperature, depth (light), clarity of water, salinity and food supply are known definitely to be of major importance, while there are others which have an influence.

Where fringing growths at shallow depth have developed around terrigenous island masses, a transient existence is not uncommon due mainly to eustatic movements, to the influence of water charged with sediment, and to the killing effect of a fresh-water layer as a result of heavy rainfalls, especially during spring tide periods. At low tide the fresh water is in contact with the coral for a period long enough to do much damage. This appears to have been the destructive element responsible for the obliteration of the once flourishing and luxuriant coral reef on Stone Island[2] in Port Denison (Bowen). Although the destruction commenced in January, 1918, even after nearly 20 years the amount of regeneration is almost negligible.

At Holbourne Island[3] (Lat. 19° 44′ S.), some 20 miles E.N.E. of Bowen, a fringing reef has been affected most adversely as a result of a small emergence, while an

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[2] Reports of Great Barrier Reef Committee, Vol. 1, 1925, pp. 35-40.

[3] *Ibid.*, pp. 29-33.

emergence of greater magnitude has been even more effective at Hunter and Iron Islands,[4] further south.

The effect of moving sand cays must be very disastrous in those reef patches where they occur. The very efficient method of ridding "green" coral of the disagreeable protoplasmic matter by burying it in coral sand for about a week is well known, and little imagination is needed to picture the results following the invasion of moving coral sand cays as a result of storm action. The movement of the Beaver Cay mass over a distance of a hundred yards in a period of a few months has been recorded definitely[5] and illustrates very well how these things go on.

Where the depths are greater the favourable conditions may be more persistent, but the results of the shallow boring operations at Low Isles[6] show that coral growths in certain regions must from time to time be buried under terrigenous sediment, with fresh growths developing later on the surface of the mud deposit.

Most people are probably disappointed on their initial landing on a coral reef to find so much "dead" coral. This, especially when covered with the algal growth *Lithothamnion*, looks very drab. They soon learn that the proportion of the reef which is flourishing and to them attractive for that reason is quite small. This relatively high percentage of "dead" coral areas on coral patches is a constant feature all along the Great Barrier Reef and in coral reef areas elsewhere.

A proper appreciation of the various factors which bring about these changes in the "life" of coral is of considerable importance, and it may be gained from the observations already made that we have to some extent at least learned to know some of them.

ORIGIN OF THE GREAT BARRIER REEF.

So many points arise in this coral reef investigation that it is difficult to prevent oneself from pursuing all kinds of interesting side lines instead of keeping on the main route.

Naturally it is important to know what is the main route; I think we may take it as being the explanation

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[4] See J. A. Steers, *Geogr. Jour.*, 1937, p. 23.

[5] T. Taylor, *Qld. Geogr. Jour.*, Vol. 39, p. 38.

[6] S. M. Marshall and A. P. Orr, Great Barrier Reef Expedition Scientific Reports (British Museum), Vol. 1, No. 5.

of why we have in the place we find it such an enormous development of coralline material.

The coral mass must rest on something, and it is clearly our duty to find out what that is. This for the lack of a better term is called the " Platform ", because there is a general belief that there is something in the nature of a platform or ledge of old rocks or " continental shelf ", perhaps more or less uniform or level, jutting out from below sea level (and coral level) to an easterly point termed the " Outer Barrier ".

What this old platform is, what its surface is like, how it was formed, and why it is now submerged, are all questions of very great importance. This is seen immediately one enters on the question of the origin of the coralline mass.

While the Great Barrier Reef area is not really a happy one in which to test out the various hypotheses as to the origin of coral reefs, at least we have to try to apply them.

Darwin's Subsidence Theory.

According to Darwin's view the " platform " represents the coastal margins of the north-eastern portions of Australia which have foundered and on which the coralline material developed and accumulated. Various factors may have played a part in modifying the form and shape of the mass, in bringing about the variation in depth of the lagoon, in establishing coral-reef patches here and there, in building up coral cays some of which become fixed by a growth of vegetation, but the essential idea is that subsidence of the coastal region has gone on. Disputes may arise as to the rate of subsidence, as to whether it has been spasmodic, or even also as to whether there have been differential amounts of subsidence due to tilting of the regions affected.

Physiographical studies by many people over a long period of time of the adjacent coastal regions have generally speaking supported the idea of subsidence. There are those who invoke faulting and warping as well, but the essential point to make clear is that on the whole the physiographers advocate some such downward movement of the region as was required by Darwin.

Other Views.

The great rival view to that of Darwin was, and perhaps still is, that of John Murray, which requires not subsidence of the area concerned, but its building up by accumulation on the sea floor to a height or shallowness of water requisite for the coral polyps to play their parts. This is regarded as being from 30–40 fathoms at the deepest.

There have been but few advocates of Murray's view as applicable to the region under consideration, but many investigators of considerable experience have been supporters of either Daly's Glacial Control Hypothesis or a modification of it.

According to Daly, during the Great Ice Age the sea level in the regions being considered was some 200–300 feet lower than at present, due to the locking up of water in a frozen condition in the higher latitudes. During this period the " platform " was cut by sea action and, when the water duly became warmer and the coral polyps established themselves, they maintained their growth upward at a rate at least equal to the 200–300 feet rise of sea level.

T. Wayland Vaughan, E. C. Andrews,[7] and a few others have postulated the formation of the antecedent platform required by the action of storms, waves and currents.

Many years earlier Andrews[8] appears to have associated the formation of the Great Barrier Reef with subsidence in late Pliocene or Pleistocene times, which in amount must have been very moderate. He went on to write " Were a bore put down in the Great Barrier Reef, it would probably show a very moderate thickness only of bedded recent or, at most, Pleistocene coral lying on mud, stones, conglomerates, and limestones of Pliocene age ".

It will be of interest a little later to consider what bearing the results of the boring operations at Michaelmas Cay, near Cairns, and at Heron Island, near Gladstone, have upon these views.

It will be quite clear from the above why many claim that the crux of the question is the origin of the foundation platform.

Without doubt any information which will give us the depth and nature of the surface of this platform is of first-rate importance, and the part which certain applied

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[7] *Jour. and Proc. Roy. Soc. N.S.W.*, 1922, Pres. Add., pp. 10-38.

[8] *Jour. and Proc. Roy. Soc. N.S.W.*, 1910, p. 420, *et seq.*

geophysical methods may play are being considered most seriously by the Committee and will be discussed later.

MICHAELMAS CAY BORE.

Many investigators, previous to the formation of the Great Barrier Reef Committee in 1923, had done much useful work, and several of its own members, such as Charles Hedley, J. A. Edgell, G. A. V. Stanley, F. Jardine, W. E. J. Paradice, and H. C. Richards had afforded much help over a period of five years by their several investigations into the physiographical, geological, and structural features of the area and mass under consideration. However, the time was considered ripe in 1928 for the carrying out of deep-boring operations to obtain, if possible, some quantitative information, especially as to the thickness of the coralline material and its make-up, and also as to the nature of the underlying material.

After much consideration of all the factors, Michaelmas Cay (Lat. 16° 36′ S., Long. 145° 59′ E.) was selected. It is not practicable to establish a boring station on the Outer Barrier, and the site selected, which is some 10 miles from the Outer Edge, is 22 miles from the coastline and about that distance N.N.E. of Cairns. The Cay is very lightly vegetated with grass, and rests on a very extensive coral reef patch developed in an area of rather luxuriant coral growth, and just to the south of the important Trinity opening through the Outer Barrier.

Forecasts were made by many in Australia and elsewhere as to what the boring results would be, but no one anticipated either the physical make-up or the thickness of the coralline material actually encountered.[9]

Some 427 feet (71 fathoms) of coralline material were passed through, and it was loosely coherent except for a total of eleven feet in the aggregate of what must be regarded as several pieces of " nigger-head material ".

From 427 feet to 600 feet (bottom of bore) loosely coherent quartz sand, in parts glauconitic and containing foraminifera and littoral shell fragments, was encountered, with no hard cemented material at all and no true coralline material recurring. Unfortunately, in the circumstances the bore could not be proceeded with, and what lies below 600 feet is not known.

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[9] Reports Great Barrier Reef Committee, Vol. 11, 1928, pp. xi-xiv.

Chemical investigation of the core material shows a complete absence of any dolomitisation, which may well have been expected on the evidence of the Funa Futi and Bahamas bores.

This bore is perhaps the first one on a coral reef which has passed through the coralline material, and the results are distinctive for :

(*a*) The loosely coherent nature of the coralline material from the surface to 427 feet ;

(*b*) the absence of dolomitisation of the coralline material.

The high percentage of foraminiferal and algal material recorded from the Funa Futi bores is found here also, and it would appear that these together form perhaps more than half of the coralline material. This was not unexpected, but the absence of dolomitisation was not in accordance with anticipations.

A very interesting feature in the results is the nature of the formation of the reef from 427 feet to 600 feet.

An examination of the material indicates that it is very similar to that encountered on beaches today in the same latitude, and it is difficult to deny the view that subsidence of at least 600 feet, or 100 fathoms, has taken place in these regions, and so it would appear that at least to that extent the general view of Darwin must be accepted.

However, no one who has examined the bore material could pretend that the coralline material has been formed *in situ* as far as a growth position is concerned for most of the material encountered. It would appear as if the "factory" was somewhere else, perhaps to seaward generally, and the disrupted fragments therefrom have been accumulated on the leeward side as it were. Of course a certain amount of material, as one may see today, has grown *in situ* as far as Michaelmas Cay is concerned.

However, whether the coralline material be *in situ* or not, and quite irrespective of what the proportion may be, the fact that subsidence of 600+ feet has taken place appears to be inescapable. The depth of the coralline material and the nature of the underlying material encountered do not fit in with the Glacial Control Hypothesis or its Antecedent Platform Hypothesis derivative, unless at the same time one is prepared to admit subsequent subsidence of considerable magnitude.

Although the surface material on the coral cays—especially the coarser material—is cemented fairly strongly, the loosely coherent nature of the material in this bore is very worthy of note especially if one bears in mind the absence of dolomitisation. Is there any relationship between these two conditions?

F. W. Clarke[10] and W. C. Wheeler have discussed the "fact that in certain groups of organisms the proportion of magnesian carbonate is dependent upon or determined by temperature". They have shown that the crinoids and alcyonarians show it very clearly, and they think perhaps the foraminifera and algæ do likewise. If this is so, boring results in the northern end of the Great Barrier Reef, where the water temperatures are higher, may furnish higher magnesium carbonate results from the same type of material.

The Commonwealth Lighthouse officials, in seeking foundation for structures on coral cays, have been most disappointed at the uncemented condition which appears the general rule immediately below the case-hardened skin of coral detritus. One must not confuse questions relating to coral rock or coral beach rock material with the one being discussed here.

The loosely coherent nature of the coralline material on the coral islands and reef-patches immediately one passes through the cemented outer skin for a foot or less is of more than ordinary interest.

As indicated earlier, at Low Isles quite a good coralline growth has been proved by shallow boring to be founded on what amounts to terrigenous mud.[11]

It would appear, therefore, that one must be prepared to find (*a*) coralline growths under conditions not hitherto regarded as suitable, and (*b*) very important and thick accumulations of coralline material uncemented and not dolomitised.

COMPOSITION OF CORAL REEFS.

The finding of such a high percentage of foraminiferal and algal material is not unexpected, and this falls into line with the Funa Futi and Bahamas coral reef material.

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[10] U.S.G.S. Prof. Paper 124, 1922, p. 61.

[11] Marshall and Orr, Great Barrier Reef Expedition Scientific Reports (British Museum), Vol. 1, No. 5.

The question does arise though as to how much coral as such is necessary to form a coral reef.

Dr. G. J. Hinde,[12] in the summary of his report on the 1,114 feet bore at Funa Futi, indicated that of the material encountered from the surface down to 180 feet "the proportion of strictly coral rock would not be more than one-fifth", the remainder being calcareous algæ, forams, etc. Between 180 and 750 feet the recovered material was small and much broken up, and so it should not be considered especially, but the recovery of core from 750–1,114½ feet was high, and speaking of the corals he writes: "Even here they appear to be considerably exceeded by the foraminiferal and fragmentary rocks." Of the material between 150–748 feet he wrote: "Both the cores and fragmentary materials largely consist of foraminifera and organic *debris*, with only a small proportion of corals."

While in London in 1935 I enjoyed the advantage of examining Dr. Hinde's slides and material, and afterwards of seeing and examining, through the courtesy of Mr. E. E. L. Dixon, of the Geological Survey, the bore material from the 395 feet bore put down in 1932 in the Bahamas by the University of Princeton Expedition. From 0–100 feet there was practically no coral at all, but the core was made up of oolitic and foraminiferal material. From 100–385 feet true coral was more or less part of the core, which was very largely foraminiferal, with many single corals through it. The coral percentage was low and appreciably lower than that from Funa Futi and from the Great Barrier Reef. From 180 feet onwards the Bahamas material is completely dolomitised and there has been much recrystallisation. Mollusc casts generally are abundant right through the whole length of the core.

It appears from the evidence of the three sets of bore results considered that coral reefs are much less strictly coral than otherwise, and so after all what are we to regard as a "coral" reef? It is clear that the true reef-building corals may be in the minority as far as bulk of the resultant reef is concerned, but one cannot have a coral reef without corals. Even if they are relatively minor in their bulk occurrence they certainly appear to be essential for the purpose of providing the very necessary framework for

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[12] Funa Futi Report, pp. 333-334.

the mass as a whole, and their existence appears to be required in providing the environment for the satisfactory development of the algæ in particular, and also perhaps for many of the forams.

A recognition of the above is necessary, especially in view of the great emphasis which in the past has been placed on the conditions as to depth, temperature, salinity food-supply, etc., necessary for the growth of corals and the effect of these on explanations as to the origin of coral reefs.

The question of what is a coral reef is quite a pertinent one to the whole matter. It seems to be quite clear that the true reef-building coral material may be decidedly in the minority even in a generally accepted coral reef.

Hitherto the limiting conditions as to coral growth have been adopted rather rigidly as applying to coral reef formation. Perhaps these need reviewing, and it may be found that in the future there should be less rigidity in this direction. Certainly the work of C. M. Yonge[13] in showing how corals may free themselves of mud was not in accord with views held generally at the time, while the amount of muddy material on which the coral growths at Low Isles were established was equally surprising.

Biological and Geographical Surveys.

Following upon the boring operations at Michaelmas Cay in 1928, the results of which have been discussed above, the great desirability of having certain marine biological and geographical work carried out became evident. Those in Australia who were competent to do such work were not available, so recourse was had to England, and a party of marine biologists, under the leadership of Dr. C. M. Yonge, came out prepared to spend a year investigating thoroughly the marine fauna and flora of the region throughout a complete cycle of the seasons.

Low Isles near Port Douglas was, for several reasons, selected as the base, although it was realised that the coral growth was not as luxuriant there as in certain other islands which had to be rejected on the score of inaccessibility or some other factor. It is essential for any party to have a reasonable base for supplies, etc., not too distant, also safety provision in the event of a cyclone was deemed

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[13] Great Barrier Reef Expedition Scientific Reports (British Museum), and "A Year on the Barrier Reef", p. 107.

essential. It is interesting to note that Low Isles, in common with many other islands considered, was visited in March, 1934, by a very destructive cyclone, and the wisdom of selecting Low Isles as the base for the Yonge party with the protection of the Lighthouse tower as well as certain other facilities was thus amply demonstrated.

As a result of observations made and experiments carried out we are now in possession of much interesting and valuable information hitherto unknown. The whole expedition from beginning to end was a great success, and the publication of the results in a series of reports by the British Museum of Natural History much enhanced the value of the work to others. But great as the work was, the fact remains that the answer to the question of how the reef was formed is still essentially a geological rather than a biological problem.

We know from other regions, and as a matter of direct observation, that the Great Barrier Reef region fulfils the necessary requirements for the faunal and floral growths necessary to build the reefs. What we require to know is what were the conditions of things when the coralline material commenced? What have been the physiographical and geological changes since? What were the geological factors in the accumulation of the material, and what mineralogical or petrological changes have been of importance as far as the resultant structures are concerned?

Whatever importance there may be attached to the biological aspects of the problem, it appears today that it is the geologist rather than the biologist who has to deal with the main questions under consideration.

Geographical investigations, especially in the way of careful mapping and description of the various coral cays and reef patches, made by Messrs. J. A. Steers and Michael Spender[14] in 1928-1929, have been extremely helpful in considering the factors responsible for the accumulation of the island patches of coral sand, their relationship to the growing coral reef patches, the movements to which the whole area has been subjected, and in facing the main question of the origin of the reef.

Steers[15] finds himself definitely on the side of those favouring submergence on a fairly extensive scale, though

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[14] J. A. Steers, *Geogr. Jour.*, Sept. and Oct., 1929.

[15] *Geogr. Jour.*, 1929, p. 239.

not necessarily of equal amount in all parts of the Barrier, and he regards the subsidence as having been due partly to simple warping and partly to faulting.

He considers[16] that the faulting and the flexing of the peneplain have been the dominant factors in the formation of the reef rather than the subsidence of the continent as a whole.

Spender maintains that shingle ramparts or ridges are the most distinctive features of island reefs (low wooded islands of the Admiralty charts). He uses the debris accumulations (cays, ramparts, shingle, etc.), on the reefs as a means of classifying them into five types, ranging from the low-lying *inner* reefs just inside the Outer Barrier up to the *island* reefs which are nearest to the mainland. He maintains that the difference between a very low *inner* reef on which the debris is scattered all over the surface and an *island* reef with its sand cay, vegetated rampart, and mangrove swamp as seen at Low Isles and Three Isles, is purely a question of difference of level.

Unquestionably the geographer can give much aid to the biologist in his ecological work on the reefs and to the geologist in several directions.

The information to be gained from detailed mapping and study of the several types of reefs is likely to be very far-reaching, and it gave much pleasure to the Committee when Mr. J. A. Steers, M.A., of Cambridge, accepted our invitation to continue his study of these coral islands last year. Accompanied by Mr. F. E. Kemp, B.A., an expert at mapping in the islands, he carried out his investigations over a wide range, but especially in the north up to Cape Direction, and in the southern end on the Bunker and Capricorn Groups.

Steers,[17] after his visit to the reefs at the northern end, found himself in agreement with Spender's classification into five types for the islands north of Port Douglas, and he described twenty-seven low wooded islands in the north. He shows that the Bunker and Capricorn islands fall into two main groups—the shingle islands and the sand islands. Heron Island, on which boring operations have recently been carried out, belongs to the latter.

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[16] *Ibid.*, p. 363.

[17] *Geogr. Jour.*, Nos. 1, 2, 1937.

Mr. Spender[18] has recently offered the opinion that deep boring should not have been undertaken again without preliminary prospecting, either with numerous shallow bores or with modern geophysical methods. He indicates that Dr. Bullard of Cambridge and Dr. Brockamp of Potsdam agree that both pendulum gravity surveys and seismic soundings could be used in the Barrier Reef area. With the latter opinions one finds himself in agreement up to a point, and the Committee has felt so for the last two or three years, but we do not yet know enough of the subcoralline make-up of the reef area to interpret correctly the results which these geophysical tests will produce.

Far and away the most valuable information the Committee has obtained has been from the Michaelmas Cay bore and from that at Heron Island. Pendulum gravity surveys, unfortunately, are not likely to be useful in telling us the thickness of the coralline material, because the results of the two deep bores do not indicate a sufficient difference in density between the overlying coralline sand material and the underlying siliceous foraminiferal sand. Whether they would tell us the depth of the underlying platform is another matter, but we have not yet been able to ascertain a means of doing that satisfactorily.

As for the seismic sounding methods, arrangements have been made tentatively for these to be carried out by either or both of the refraction and reflection methods as conditions require, but it was decided after mature consideration to carry out the deep boring before applying these tests.

The results of the Heron Island bore have shown the wisdom of this, as the presence of certain very hard bands well below the coralline material and above the underlying platform will introduce elements which may be disconcerting. Even if these difficulties are surmounted, the trouble will be to say how much of the superincumbent material above the underlying platform is coralline, and how much is the siliceous sands met under the coral in both deep bores.

The use of these methods after the deep boring is much to be desired, and the Committee hopes to avail itself of their help subsequently.

To date the only definite quantitative information we have as to the reef's thickness, its physical make-up, and its underlying material has been derived from the deep bores.

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[18] *Geogr. Jour.*, No. 2, 1937, p. 142.

HERON ISLAND BORE.

In conclusion, the results of the boring at Heron Island (Lat. 23° 26′ S., Long. 151° 57′ E.), some 48 miles E.N.E. of Gladstone, are of considerable interest.

Heron Island is 10 miles from the 100 fathom line and 44 miles from the mainland. The water in the channels about the island reaches a depth of 26 fathoms, and the Heron Island reef-patch is some seven miles in length and two miles in width. The sand cay is on the western end, and is approximately one mile in circumference.

Boring operations (17/7/37) have reached a depth of 567 feet, having commenced in coral sand. From 17–22 feet coral beach rock of a somewhat cemented nature was met, but until a depth of 512 feet was reached there was nothing sufficiently strongly cemented to furnish a solid core, and the percussion method with a drive pump and cutting shoe was adopted.

From the surface to about 450 feet coralline material has been encountered, more or less loosely coherent and with abundant foraminiferal and algal remains. At 292–294 feet a band of loosely coherent fine white silica sand was passed, but all else from surface to 450 feet or thereabouts was coralline. From then on to 567 feet siliceous sand with forams, and fragments of shallow water shells, has been encountered with occasional bands of hard calcareous sandstone. Sometimes the foraminiferal material is sufficiently abundant to make the calcium carbonate the dominant material and sometimes the quartz grains predominate. The quartz sands are loosely coherent and the harder calcareous bands are sometimes 18 inches or so thick.

One band at 511 feet is exceedingly hard and over a foot thick. What effect it would have in seismic reflection tests would be of considerable interest to us.

The nature of the sands at 567 feet is such as one finds associated with the weathered material from the old metamorphosed palæozoic sediments on the mainland.

To some extent glauconitic material in the foram casts occur in the sub-coralline quartz sands.*

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* A total depth of 732 feet was reached before technical difficulties forced a discontinuance of operations. Occasional foraminiferal siliceous limestone bands of varying thickness in loosely coherent quartz beach sand material persisted right through. No true coralline material whatever was encountered below approximately 450 feet.

The remarkable similarity in the Michaelmas Cay and Heron Island bores as to the thickness and physical make-up of the coralline material, and also of the nature of the sub-coralline material is a matter of considerable interest. It is difficult to think that it is just a coincidence. The bearing of these two sets of very similar results on one's ideas as to the nature and the amount of the movements is most important. The conclusions on these matters arrived at for Michaelmas Cay appear to have their full endorsement at Heron Island.

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THE VIRTUAL GENUS OF A CURVE WITH A MULTIPLE POINT.

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(*Manuscript received, July 10, 1937. Read, August 4, 1937.*)

The objects of this note are (i) to establish a theorem which will facilitate the calculation of the genus of a curve c from that of a special curve c' whose genus is known, the specification of c' differing from that of c only in that c' has an additional multiple point, and (ii) to apply the theorem to the calculation of the genus of the double curve on a determinantal primal in [5].[1] At the end of the note an extension of the theorem is suggested to manifolds of dimension greater than one.

1. The Deduction of the Theorem from a Theorem of Noether's.

The theorem to be proved is similar in form to Noether's classical theorem, namely[2]:

Theorem A. If c' and c'' are two curves having r common points, and are together equivalent to a curve c, the genera of the curves being respectively p', p'', and p, then

$$p=p'+p''+r-1.$$

The term "equivalent" is to be taken to mean that there exists a surface on which c and $c'+c''$ are coresidual. The theorem which is proposed is:

Theorem B. A surface Σ has an isolated multiple point G at which the tangent cone is Γ[3]; c is the section of Σ by a general prime, and c' its section by a general prime through G.

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[1] The terminology throughout is that of Baker: "Principles of Geometry", Vols. 1-6, Cambridge, 1922-1933.

[2] Noether: *Rend. di Palermo*, 1886, *13*, 344. See, e.g., Enriques-Chisini: "Teoria Geometrica delle Equazioni", 3 (Bologna, 1924), 400, or Baker: *l.c.* 5, 209, footnote.

[3] It is assumed that G is a multiple point of sufficiently general character, i.e., roughly that Γ is irreducible, and its general section by a prime through G consists of r distinct lines, each a simple tangent to a branch of the curve in which the prime cuts Σ.

If p, p', and π are respectively the genera of c, c', and a general prime section of Γ, and r is the order of Γ, then

$$p = p' + \pi + r - 1.$$

Theorem B can be deduced directly from theorem A thus; transform Σ birationally by means of a family of primals which has G as a simple isolated base point into a surface Σ^* on which G is represented by a curve γ^*, and c and c' by c^* and c'^*. Then the curves have these properties: γ^* has the same genus as a general prime section of Γ, c^* and c'^* have the same genera as c and c', c'^* meets γ^* in r points corresponding to the r-ple point of c' at G, and c^* is equivalent to $c'^* + \gamma^*$.

2. The Scope of Theorem B.

Theorem B is more restricted in scope than theorem A, since, whilst all simple curves equivalent to $c' + c''$ have the same genus, simple curves of different genera can be found equivalent to a given curve c' under the conditions of theorem B.[4] In theorem A the number p is characteristic of the composite curve $c' + c''$; it is the postulation genus.[5] But the only property that p has in relation to the curve c' of theorem B is that it is less than or equal to the postulation genus.

This restriction on the scope of the theorem does not invalidate the use of the theorem for the purpose set out at the beginning of the note, namely that of calculating from properties of c' the genus of c, when both curves are given as prime sections of the same surface.

As an example of a curve c' for which two different values of p can be found, take an elliptic curve in [3] of order 7 with a 4-ple point G, namely the residual intersection of two cubic surfaces with a common node (at G), and a common conic not through G. The two surfaces Σ_1 and Σ_2 defined below both have curves of the same specification as c' as their general prime sections through their 4-ple points, while their sections by primes not through the 4-ple points have genera 5 and 4 respectively. The

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[4] Such a restriction is to be expected, since, e.g., a quartic curve in [3] with a double point is coresidual on a quadric surface both with a (2, 2) curve for which $p=1$, and with a (1, 3) curve for which $p=0$. An example is given below of two curves equivalent under the conditions of theorem B to the same curve, but having different genera.

[5] If p is the postulation genus of a curve of order n, then the number of conditions imposed on primals of sufficiently high order n', in making them contain the curve, is $nn' - p + 1$.

postulation genus of c' is 5; there are, e.g., ∞^2 cubic surfaces through the curve.

(i) Σ_1 is the surface in [4] whose general prime sections, c_1, are represented by plane curves of order 6, with 5 double base points D', and 8 simple base points all lying on a cubic curve γ'^3 (so that the eighth simple base point is determined by the points D' and the other 7 simple base points), and one other simple base point A'. γ'^3 represents a 4-ple point G on the surface, the tangent cone at which is elliptic, and the prime sections, c'_1, through G are represented by cubic curves passing simply through A' and the 5 points D'. For c'_1 and c_1

$$p'=1, \quad r=4, \quad p=5, \quad \pi=1.$$

The sets of the canonical series g^8_4 on c_1 are cut out by the ∞^4 quadric surfaces in the solid containing the curve, which pass through a 6-secant conic of the curve. On c'_1 this series is replaced by that cut out by the ∞^3 quadric surfaces through the 4-ple point G on the curve, as well as a 6-secant conic.

(ii) Σ_2 is the surface in [4] whose general prime sections, c_2, are represented by plane curves of order 5 with 5 simple base points on a line g' (which represents a 4-ple point G on the surface, at which the tangent cone is rational), 5 other simple base points A', and 2 double base points D'. A prime section, c'_2, through G is represented by a quartic curve through the 5 points A', and having double points at the 2 points D'. For c'_2 and c_2

$$p'=1, \quad r=4, \quad p=4, \quad \pi=0.$$

Σ_2 has on it 2 plane quartic curves, each with a triple point at G; each is represented by the single cubic curve which has a double point at one point D', and simple points at the other point D' and at the 5 points A'.[6] The canonical series g^6_3 on any curve c_2 is cut out by the ∞^3 quadric cones vertex G through the planes of the two quartic curves; i.e. the surfaces in the solid containing the curve which cut out the series are the quadrics through the two 4-secant lines. The series corresponding on c'_2 is thus cut out by the quadric cones (surfaces) vertex at the 4-ple point of the curve, and containing 2 lines through

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[6] The section of one of these planes by a prime is a line which is 4-secant to the curve c_2 in the prime. A curve of order 7 and genus 4 has 2 4-secant lines (Baker: l.c., 6, 34) and thus there are no 4-secant lines of c_2 other than the sections of these 2 planes. I.e., all 4-secant lines of Σ_2 lie in the two planes.

that point which meet the curve again. The variable part of this series is identical with that on c'_1.

3. The Genus of the Double Curve on a General Determinantal Primal in [5].

Denote by D^q_{n-1} the primal in $[n]$ represented by the equation

$$|\, x_{\alpha\beta} \,| = 0 \qquad \begin{array}{l} \alpha=1,\ldots,\ q \text{ along rows} \\ \beta=1,\ldots,\ q \text{ down cols.,} \end{array}$$

where the $x_{\alpha\beta}$ are linear functions of the coordinates in $[n]$, and denote by $\Delta^{(q)}_{n-4}$ the manifold of dimension $n-4$ and order $N=\frac{1}{12}q^2(q^2-1)$ represented by the vanishing of all first minors of the determinant.[7]

$\Delta^{(q)}_{n-1}$ is double on D^q_{n-1}. It is to be proved that:

The genus of the curve $\Delta_1^{(4)}$ *in [5] is 21.*

The same method may be applied inductively to prove that:

The genus of the curve $\Delta_1^{(q)}$ *in [5] is* $(q-3)N+1$.

Let MD_5^4 be the quartic determinantal monoid in [6] represented by the equation

$$\begin{vmatrix} x_{\alpha\beta}\cdot & x_{4\beta} \\ x_{\alpha 4}, & x_0 \end{vmatrix} = 0 \qquad \alpha,\ \beta=1,\ 2,\ 3,$$

where the 15 quantities $x_{\alpha\beta}$, $x_{4\beta}$, $x_{\alpha 4}$ are functions of the coordinates $x_1, \ldots, x_6$ in the space, but not of x_0. MD_5^4 has a triple point at the vertex A_0 of the simplex of reference (opposite the prime $x_0=0$), and the double surface $M\Delta_2^{(4)}$ on MD_5^4 has at A_0 a point the multiplicity, r, of which is to be found. The surface $M\Delta_2^{(4)}$ satisfies the conditions of theorem B; thus if c is a general prime section of the surface (i.e. is a general curve $\Delta_1^{(4)}$), and c' is the section by a prime through A_0, the difference of the genera of these curves is given by

$$p-p'=\pi+r-1,$$

where π is the genus of the general prime section of the tangent cone to $M\Delta_2^{(4)}$ at A_0, and r is its order. We proceed to calculate p', π, and r.

The tangent cone to MD_5^4 at A_0 is

$$|\, x_{\alpha\beta} \,| = 0, \qquad \alpha,\ \beta=1,\ 2,\ 3,$$

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[7] This formula for the order is to be found. e.g., in Baker, l.c., 6, 110, with $\mu=1$, $p=q=c+1$, and q of his account replaced in the account above by $q-1$.

and that to $M\Delta_2^{(4)}$ is represented by the vanishing of the first minors of this determinant. The general prime sections of these cones are thus a general primal D_3^3 in [4], and the double curve $\Delta_1^{(3)}$ on that primal. $\Delta_1^{(3)}$ is a curve of order 6, namely $\frac{1}{12}3^2(3^2-1)$, and genus 1(8) so that, of the numbers above, $r=6$, and $\pi=1$.

We may suppose that the prime through A_0 by which the section of MD_5^4 is taken is $x_6=0$; then the equations of c' are

$$\left\| \begin{matrix} x'_{\alpha\beta}, & x'_{4\beta} \\ x'_{\alpha 4}, & x_0 \end{matrix} \right\|_2 = 0,$$

where $x'_{\alpha\beta}, \ldots$ are the functions $x_{\alpha\beta}, \ldots$ with x_6 put equal to zero. The equations of the projection of c' from A_0 on to a [4] are obtained by eliminating x_0 from this system; the resulting equations are:

$$\| x'_{\alpha\beta}, \quad x'_{4\beta} \|_2 = 0, \qquad \left\| \begin{matrix} x'_{\alpha\beta} \\ x'_{\alpha 4} \end{matrix} \right\|_2 = 0$$

These represent the curve common to two Bordiga surfaces of opposite systems on a primal D_3^4 in [4].[9]

When D_3^4 is represented on a [3] by quartic surfaces through a curve h' of order 10 and genus 11, the Bordiga surfaces of one system are represented by planes, and those of the other by surfaces of order 11 on which h' is triple. The curve of intersection of a plane and one of the surfaces is of order 11 with 10 triple points, and is therefore of genus 15. Thus the genus of the curve common to the Bordiga surfaces, and therefore also of the curve c' of which it is a projection, is 15. I.e.,

$$p'=15, \quad \pi=1, \quad r=6,$$

and therefore $p=21$.

4. A Possible Extension of Theorem B.

Severi's tentative generalization of theorem A[10] suggests the following generalization of theorem B.

Theorem C. *A* $(d+1)$*-fold,* Σ_{d+1}*, has an isolated multiple point* G *(of sufficiently general type) at which the tangent cone is* Γ_{d+1}. V_d *is the section of* Σ_{d+1} *by a general prime, and*

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[8] See, e.g., Veneroni: *Rend. R. Ist. Lombardo*, 1905, *38* (2), 523.

[9] See, e.g., Roth: *Proc. London Math. Soc.*, 1930, *30* (2), 118-126 (119).

[10] Severi: *Rend. di Palermo*, 1909, *28*, 33-87 (41).

V'_d the section by a general prime through G. If p_d, p'_d, π_d, π_{d-1} are respectively the numerical genera of V_d, V'_d, a general prime section of Γ_{d+1}, and a general secundum section of Γ_{d+1}, then

$$p_d = p'_d + \pi_d - \pi_{d-1}.$$

The numerical genus of a manifold of dimension greater than one is not a proper invariant, so that the method adopted in §1 for curves will not lead to a proof, unless it can be shown that the various additional terms, that arise when the manifolds on Σ_{d+1} are transformed into manifolds on Σ^*_{d+1}, cancel out.

PYRROLES DERIVED FROM ACETONYLACETONE.

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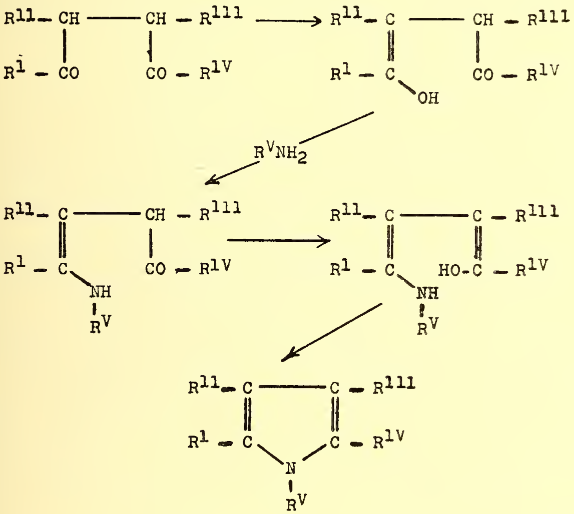
Of the methods available for the synthesis of derivatives of pyrrole, one of the oldest and most generally applicable is the Paal-Knorr Synthesis (Knorr, *Berichte*, 1885, *18*, 302; *Annalen*, 1886, *236*, 290; Paal, *Berichte*, 1885, *18*, 367, 2251) in which γ-diketones are condensed with ammonia or primary amines. Much work on this reaction has established that practically any 1: 4-diketone capable of forming a di-enol may be used with ammonia; that not all primary amines are suitable; and that acid amines do not react to give N-acyl pyrroles at all. Thus, Paal and Schneider (*Berichte*, 1886, *19*, 3156) examined the behaviour of acetonylacetone and phenacylacetoacetic ester towards certain substances containing the $-NH_2$ group and showed that they condensed readily with ethylene diamine, trimethylenediamine, m-phenylenediamine, benzidine, glycine, m-aminobenzoic acid, o-aminophenol, and aminoazobenzene, but failed to give pyrroles with urea, oxamide, benzamide, o-nitraniline or sulphanilic acid. They concluded that pyrrole formation would occur only if the amines used were of strong basic character.

That the problem is not so simple as this, however, is shown by later observations of Paal and Braikoff (*Berichte*, 1889, *22*, 3086-95), who found that ethyl phenacyl benzoylacetate condenses readily with aromatic amines such as aniline, o- and p-toluidines, 4-m-xylidine, α- and β-naphthylamines, o-aminophenol and p-phenylenediamine, but fails to give pyrroles with such relatively strong aliphatic bases as ethylamine, allylamine and ethylene diamine. It also fails to give pyrroles with glycine and m-aminobenzoic acid.

These two series of experiments show clearly that the factors governing the formation of pyrroles depend partly on the diketone employed and partly on the amine. That the strength of the amine as a base is not the only factor is also indicated by the work of Borsche and Titsingh (*Berichte*, 1907, *40*, 5011), who studied the condensation of ethyl phenacyl acetoacetate with the isomeric nitroanilines, and found that whereas p- and m-nitroanilines could condense to give good yields of the corresponding l-nitrophenyl pyrroles, o-nitroaniline condensed only with great difficulty, the yield of pyrrole being very bad even after several day's heating of the components together in glacial acetic acid solution.



It is probable that in the Paal-Knorr reaction the diketone first reacts as a mono-enol with the ammonia or amine present to give an intermediate unsaturated γ-amino ketone. Subsequent enolization of the second ketone group followed by intramolecular linkage of carbon with nitrogen and simultaneous extrusion of a water molecule completes the ring closure.

The intermediate γ-amino ketone may sometimes be isolated by adopting special precautions. Thus, Knorr and Rabe (*Berichte*, 1900, *33*, 3801) isolated 2-amino-$\triangle^2$-hexen-5-one-3 : 4-dicarboxylic diethyl ester by the action of ammonia on diethyl diacetyl succinate in ice-cold ethereal solution. Borsche and Fels (*Berichte*, 1906, *39*, 3877), also, have isolated similar intermediates from ethyl phenacyl acetoacetate and from ethyl acetonylbenzoyl acetate.

If the suggested mechanism for the reaction be the true one it might be expected that the early stages of pyrrole formation will be influenced by the degree to which the diketone employed is enolized, and a good deal of attention must be paid to this aspect of the problem in any systematic study of the reaction.

Recent investigation of the by-products obtained in the manufacture of acetic acid from acetylene on the large scale has shown that acetonylacetone is one of the substances produced in the process, and that it accumulates in the high boiling fractions (cf. Benson and Cadenhead, *J. Soc. Chem. Ind.*, 1934, *53*, 40–43). In consequence, acetonylacetone has become available in quantity and is now a relatively cheap organic chemical. The arrival of a supply of this simplest γ-diketone has led us to study its condensation with a large number of amines—mainly aromatic—in order to ascertain whether those amines which resist pyrrole formation with it have any significant property in common. In the course of these experiments we have studied the conditions of condensation, and have worked out a useful variation of the method usually utilised by the earlier workers, who heated the components together in glacial acetic acid solution. Following up an observation of Coffey, Thomson, and Wilson (*J.C.S.*, 1936, 856) that acid catalyses the condensation of amines with acetoacetic ester to β-aminocrotonic esters we have found that an equimolecular mixture of acetonylacetone and an aromatic amine such as aniline splits out water very rapidly after addition of a very small amount of 1 : 1 hydrochloric acid and gentle warming. However, the mineral acid seems to help polymerization, and the products rapidly become red. Boiling glacial acetic acid also causes darkening, when the condensation is carried out in this medium. However, if the components are boiled under reflux in alcoholic solution in presence of a little glacial acetic acid the pyrrole condensation goes quite smoothly, the products are much cleaner, and the yields are good.

Repetition of the experiments of some previous workers has confirmed their observations. Thus, we have confirmed Paal and Schneider's result (*loc. cit.*) that urea and o-nitroaniline fail to give any trace of a pyrrole with acetonylacetone, even under widely varied conditions. Tribromoaniline also fails to react and this result may possibly be attributed to steric hindrance, but ortho substituted anilines do not, in general, show any marked reluctance to form pyrroles (cf. Holdsworth and Lions, *Journ. Roy. Soc. N.S.W.*, 1936, *70*, 431-6). 2 : 4-Dichloroaniline, also, apparently fails to react.

The most interesting failure we have encountered is that of methyl anthranilate, which gave no pyrrole even under the most widely varied conditions. Anthranilic acid itself reacts very readily with acetonyl acetone to form l-o-carboxyphenyl-2 : 5-dimethyl pyrrole in good yield. Also, Bock and Adams (*J.A.C.S.*, 1931, *53*, 374) heated ethyl acetonyl acetoacetate and anthranilic acid together in alcoholic solution and obtained a 30 per cent. yield of ethyl 1-o-carboxyphenyl-2 : 5-dimethyl pyrrole-3-carboxylate within an hour. Anthranilic acid also condenses readily with phenacyl lævulinic acid to l-o-carboxyphenyl-2-phenyl pyrrole 5-β-propionic acid (Holdsworth and Lions, *loc. cit.*). An attempt to condense o-amino benzamide with acetonyl acetone gave no readily isolable pyrrole, and an attempt to condense an o-aminoacetophenone derivative—6-aminoacetoveratrone—with acetonyl acetone was also a failure. We further attempted the condensation of methyl anthranilate with ethyl phenacyl acetoacetate and with phenacyl lævulinic acid without success. The theoretical implications of these failures will be discussed later, when more data has been accumulated. The pyrroles prepared are described below in the experimental section.

EXPERIMENTAL.

Two general methods were employed for the preparation of the derivatives of pyrrole described below.

(A) The amine (approximately 3 grams) was mixed with a slight excess of acetonyl acetone, warming if necessary to obtain a homogeneous solution, and then one small drop of 5N hydrochloric acid was added. When reaction proceeded at room temperature, which was indicated by the almost immediate separation of water globules, the reaction mixture was allowed to stand for about 30 minutes before being worked up. If there was no rapid separation of water the mixture was heated at 100° for periods varying between one and two hours, according to the rapidity of separation of water globules, and was then cooled. If the product of reaction crystallised it was usually dried on a porous plate and was then recrystallised. Otherwise, it was poured into water, taken up and dried in ether, and, if necessary, distilled under reduced pressure.

(B) Equimolecular quantities of the base (3 grams approximately) and acetonyl acetone were dissolved in a mixture of ethyl alcohol (10 c.c.) and glacial acetic acid (1 c.c.) and the solution then heated under reflux for periods varying between 15 minutes and 4 hours. After cooling, the reaction mixture was poured into water, and the product recovered as in method A.

The yields obtained by both these methods were usually very good. However, the products from method B were usually much cleaner and this method is to be preferred. In method A, after a certain time the product rapidly tends to redden, and it is worthy of note that very few of the pyrroles obtained are particularly stable when exposed to light and air.

1-Phenyl-2 : 5-dimethyl pyrrole.

From aniline and acetonyl acetone. Method A. Recrystallised from methyl alcohol m.p. 51–52°. This substance has been previously prepared by the decarboxylation of l-phenyl-2 : 5-dimethyl pyrrole-3 : 4-dicarboxylic acid (Knorr, *Annalen*, *236*, 308).

1-o-Tolyl-2 : 5-dimethyl pyrrole.

From o-toluidine and acetonyl acetone. Method B. Colourless liquid boiling at 123–125°/22 mm. Found N=7·8%; calculated for $C_{13}H_{15}N$, N=7·6%.

1-m-Tolyl-2 : 5-dimethyl pyrrole.

From m-toluidine and acetonyl acetone. Method B. Recrystallised from methyl alcohol as glistening plates m.p. 55°. This substance has been previously prepared by the decarboxylation of l-m-tolyl-2 : 5-dimethyl pyrrole-3 : 4-dicarboxylic acid (Bulow, List, *Berichte*, 1902, *35*, 688).

1-p-Tolyl-2 : 5-dimethyl pyrrole.

From p-toluidine and acetonyl acetone. Method A. Recrystallised from methyl alcohol as glistening plates m.p. 46°. This substance has been previously prepared by the decarboxylation of 1-p-tolyl-2 : 5-dimethyl pyrrole-3 : 4-dicarboxylic acid (Knorr, *Berichte*, 1885, *18*, 309).

1-(2 : 4-Dimethyl phenyl)-2 : 5-dimethyl pyrrole.

From 4-m-xylidine and acetonyl acetone. Method B. Colourless fragrant liquid boiling at 136°/10 mm. Found N=7·1%; calculated for $C_{14}H_{17}N$, N=7·0%.

1-(2 : 5-Dimethyl phenyl)-2 : 5-dimethyl pyrrole.

From p-xylidine and acetonyl acetone. Method B. Colourless fragrant liquid boiling at 121°/9 mm. Found N=7·2%; calculated for $C_{14}H_{17}N$, N=7·0%.

1-(3′-Acenaphthyl)-2 : 5-dimethyl pyrrole.

From 3-amino acenaphthene and acetonyl acetone. Method B. Recrystallised from ethyl alcohol as faintly brown crystals m.p. 92°. Found N=5·8%; calculated for $C_{18}H_{17}N$, N=5·7%.

1-(3′-Fluorenyl)-2 : 5-dimethyl pyrrole.

From 3-amino-fluorene and acetonyl acetone. Method B. Recrystallised from ethyl alcohol as pink needles m.p. 90–91°. Found N=5·4%; calculated for $C_{19}H_{17}N$, N=5·4%.

1-(α-Naphthyl)-2 : 5-dimethyl pyrrole.

From α-naphthylamine and acetonyl acetone. Method A. Recrystallised from methyl alcohol m.p. 121°. This substance has been previously prepared by the decarboxylation of 1-α-naphthyl-2 : 5-dimethyl pyrrole-3 : 4-dicarboxylic acid (Knorr, *Annalen*, *236*, 308).

1-(β-Naphthyl)-2 : 5-dimethyl pyrrole.

From β-naphthylamine and acetonyl acetone. Method A. Recrystallised from methyl alcohol m.p. 71°. This substance has been previously prepared by the decarboxylation of 1-β-naphthyl-2 : 5-dimethyl pyrrole-3 : 4-dicarboxylic acid (Knorr, *Annalen*, *236*, 306).

1-Ethyl-2 : 5-dimethyl pyrrole.

From ethylamine and acetonyl acetone—reaction proceeded without addition of catalyst. Method A. Colourless liquid boiling at 102°/79 mm. Found N=11·6%; calculated for $C_8H_{13}N$. N=11·4%.

1-(α-Phenyl ethyl)-2 : 5-dimethyl pyrrole.

From α-phenyl ethylamine and acetonyl acetone. Method B. Distilled at 147–149°/14 mm. and then solidified. Recrystallised from alcohol, colourless prisms m.p. 53°. Found N=7·3%; calculated for $C_{14}H_{17}N$, N=7·5%.

1-Benzyl-2 : 5-dimethyl pyrrole.

From benzylamine and acetonyl acetone. Method A. Recrystallised from aqueous alcohol as colourless needles m.p. 48°. Found N=7·7%; calculated for $C_{13}H_{15}N$, N=7·5%.

1-(o-Xenyl)-2 : 5-dimethyl pyrrole.

From o-xenylamine and acetonyl acetone. Method A. Recrystallised from methyl alcohol as colourless plates m.p. 100°. Found N=5·6%; calculated for $C_{18}H_{17}N$, N=5·7%.

1-(p-Xenyl)-2 : 5-dimethyl pyrrole.

From p-xenylamine and acetonyl acetone. Method B. Recrystallised from methyl alcohol m.p. 65°. Found N=5·4%; calculated for $C_{18}H_{17}N$, N=5·7%.

1-o-Chlorophenyl-2 : 5-dimethyl pyrrole.

From o-chloroaniline and acetonyl acetone. Method B. Colourless liquid boiling at 135°/15 mm. Found N=6·8%; calculated for $C_{12}H_{13}NCl$, N=6·8%.

1-m-Chlorophenyl-2 : 5-dimethyl pyrrole.

From m-chloroaniline and acetonyl acetone. Method B. Recrystallised from methyl alcohol as colourless needles. m.p. 50°. Found N=7·0%; calculated for $C_{12}H_{13}NCl$, N=6·8%.

1-m-Bromphenyl-2 : 5-dimethyl pyrrole.

From m-bromaniline and acetonyl acetone. Method A. Recrystallised from methyl alcohol m.p. 83°. Found N=5·7%; calculated for $C_{12}H_{13}NBr$, N=5·6%.

1-p-Bromphenyl-2 : 5-dimethyl pyrrole.

From p-bromaniline and acetonyl acetone. Method A. Recrystallised from aqueous methyl alcohol as grey crystals m.p. 74–75°. Found N=5·6%; calculated for $C_{12}H_{13}NBr$, N=5·6%.

1-(2 : 5-Dichlorphenyl)-2 : 5-dimethyl pyrrole.

From 2 : 5-dichloraniline and acetonyl acetone. Method B. Pale yellow liquid boiling at 151–153°/16 mm. Found N=5·9%; calculated for $C_{12}H_{12}NCl_2$, N=5·8%.

1-(m-Hydroxyphenyl)-2 : 5-dimethyl pyrrole.

From m-aminophenol and acetonyl acetone. Method B. Distilled at 178°/10 mm. and solidified on cooling m.p. 58°. Found N=7·6%; calculated for $C_{12}H_{13}NO$, N=7·5%.

1-(o-Methoxy phenyl)-2 : 5-dimethyl pyrrole.

From o-anisidine and acetonyl acetone. Method B. Recrystallised from methyl alcohol as white needles m.p. 65°. Found N=7·0%; calculated for $C_{13}H_{15}ON$, N=7·0%.

1-(p-Methoxy phenyl)-2 : 5-dimethyl pyrrole.

From p-anisidine and acetonyl acetone. Method A. Recrystallised from methyl alcohol as white needles m.p. 65°. Found N=7·0%; calculated for $C_{13}H_{15}ON$, N=7·0%.

1-(o-Ethoxy phenyl)-2 : 5-dimethyl pyrrole.

From o-phenetidine and acetonyl acetone. Method B. Pale yellow liquid boiling at 140°/10 mm. Found N=6·3%; calculated for $C_{14}H_{17}NO$, N=6·5%.

1-(p-Ethoxy phenyl)-2 : 5-dimethyl pyrrole.

From p-phenetidine and acetonyl acetone. Method A. Recrystallised from methyl alcohol as colourless plates m.p. 63°. Found N=6·6%; calculated for $C_{14}H_{17}NO$, N=6·5%.

1-(2 : 3-Dimethoxy phenyl)-2 : 5-dimethyl pyrrole.

From 3-amino veratrole and acetonyl acetone. Method B. Recrystallised from aqueous alcohol as white needles m.p. 68°. Found N=5·8%; calculated for $C_{14}H_{17}NO_2$, N=6·1%.

1-(3 : 4-Dimethoxy phenyl)-2 : 5-dimethyl pyrrole.

From 4-amino veratrole and acetonyl acetone. Method B. Recrystallised from alcohol as needles m.p. 54–55°. Found N=5·9%; calculated for $C_{14}H_{17}NO_2$, N=6·1%.

1-(3 : 4-Diethoxy phenyl)-2 : 5-dimethyl pyrrole.

From 4-amino catechol diethyl ether and acetonyl acetone. Method B. Colourless liquid boiling at

204–205°/34 mm. Found N=5·5%; calculated for $C_{16}H_{21}NO_2$, N=5·4%.

1-(m-Nitro phenyl)-2 : 5-dimethyl pyrrole.

From m-nitraniline and acetonyl acetone. Method B. Required approximately two hours heating. Recrystallised from methyl alcohol as large yellow prisms m.p. 84–85°. Found N=13·1%; calculated for $C_{12}H_{12}N_2O_2$, N=13·0%.

1-(p-Nitro phenyl)-2 : 5-dimethyl pyrrole.

From p-nitraniline and acetonyl acetone. Method B. Recrystallised from methyl alcohol as yellow plates m.p. 145°. Found N=12·9%; calculated for $C_{12}H_{12}N_2O_2$, N=13·0%.

1-(2-Methyl-5-nitro-phenyl)-2 : 5-dimethyl pyrrole.

From p-nitro-o-toluidine and acetonyl acetone. Method B. Recrystallised from alcohol as golden-yellow crystals m.p. 103–104°. Found N=11·8%; calculated for $C_{13}H_{14}N_2O_2$, N=12·2%.

1-o-Carboxy phenyl-2 : 5-dimethyl pyrrole.

From antranilic acid and acetonyl acetone. Method B. Heated for three hours. Recrystallised from ligroin as colourless plates m.p. 121–122°. Found N=6·9%: calculated for $C_{13}H_{13}NO_2$, N=6·5%.

1-(m-Carboxy phenyl)-2 : 5-dimethyl pyrrole.

From m-aminobenzoic acid and acetonyl acetone. Method A. Recrystallised from methanol as faintly pink plates m.p. 146° (previous recorded 134–135° Paal Schneider, *Berichte*, *19*, 559). Found N=6·4%; calculated for $C_{13}H_{13}NO^2$, N=6·5%.

1-(p-Carboxy phenyl)-2 : 5-dimethyl pyrrole.

From p-aminobenzoic acid and acetonyl acetone. Method A. Recrystallised from methyl alcohol as faintly pink plates m.p. 196–198°. Found N=6·4%; calculated for $C_{13}H_{13}NO_2$, N=6·5%.

1-(p-Carbethoxy phenyl)-2 : 5-dimethyl pyrrole.

From ethyl p-amino benzoate and acetonyl acetone. Method A. Recrystallised from methyl alcohol as white needles m.p. 87–88°. Found N=5·8%; calculated for $C_{15}H_{17}NO_2$, N=5·8%.

1-1′-m-Phenylene-bis-(2 : 5-dimethyl pyrrole).

From m-phenylene diamine and acetonyl acetone two molecular parts. Method A. Recrystallised from alcohol as white plates m.p. 106–107°. Found N=10·5%; calculated For $C_{18}H_{28}N_2$, N=10·6%.

1-(m-Acetamido phenyl)-2 : 5-dimethyl pyrrole.

From m-amino acetanilide and acetonyl acetone. Method B. Recrystallised from methyl alcohol as faintly brown plates m.p. 192°. Found N=12·9%; calculated for $C_{14}H_{17}N_2O$, N=12·3%.

1-1′-p-Phenylene-bis-(2 : 5-dimethyl pyrrole).

From p-phenylene diamine and acetonyl acetone two molecular parts. Method A. Recrystallised from benzene as white plates softening at 245°, m.p. 253°. Found N=10·4%; calculated for $C_{18}H_{20}N_2$, N=10·6%.

1-(p-Acetamido phenyl)-2 : 5-dimethyl pyrrole.

From p-amino acetanilide and acetonyl acetone. Method A. Recrystallised from methyl alcohol as faintly pink plates m.p. 207°. Found N=12·6%; calculated for $C_{14}H_{17}N_2O$, N=12·3%.

1-1′-(3-3′-dimethyl diphenylene (4-4′))-bis-(2 : 5-dimethyl pyrrole).

From o-tolidine and acetonyl acetone two molecular parts. Method A. Recrystallised from dioxan m.p. 190°. Found N=7·8%; calculated for $C_{26}H_{28}N_2$, N=7·6%.

1-(5′-Quinolinyl)-2 : 5-dimethyl pyrrole.

From 5-aminoquinoline and acetonyl acetone. Method A. Recrystallised from methyl alcohol m.p. 77°. Found N=12·6%; calculated for $C_{17}H_{14}N_2$, N=12·6%.

1-(8′-Quinolinyl)-2 : 5-dimethyl pyrrole.

From 8-amino quinoline and acetonyl acetone. Method A. Recrystallised from methyl alcohol as pink plates m.p. 143°. Found N=12·8%; calculated for $C_{17}H_{14}N_2$. N=12·6%.

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SOME DERIVATIVES OF HIGHER CATECHOL ETHERS.

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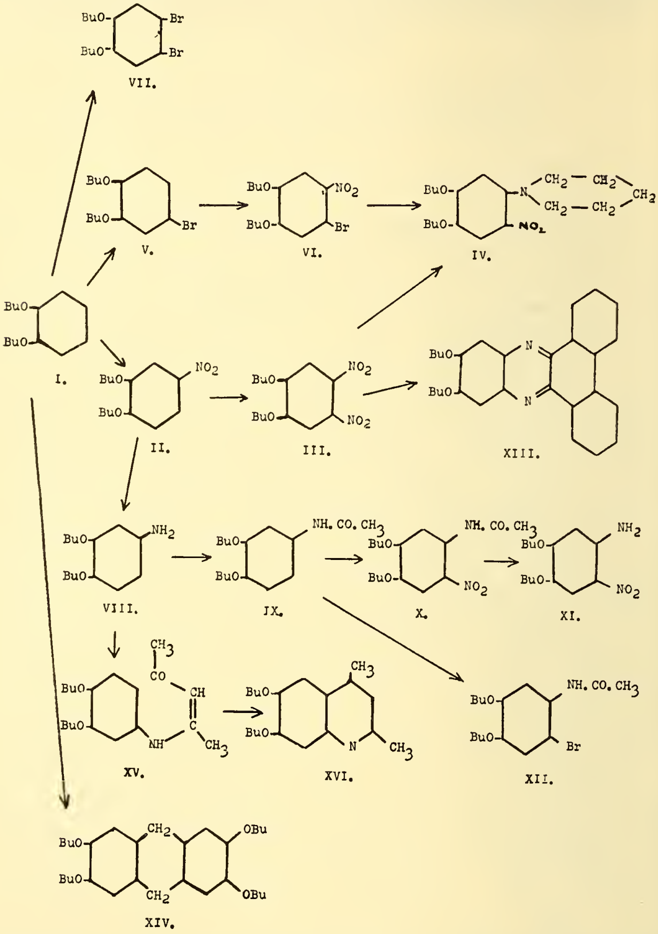
An attempt to sulphonate catechol di-n-butyl ether with chloro-sulphonic acid by the method used by Brown and Robinson (*J.C.S.*, 1917, 953) elicited the fact that this ether is dealkylated under the experimental conditions with great readiness, and it was not possible to isolate any of the expected sulphon chloride. Further experiments with concentrated sulphuric acid showed that this reagent also can cause loss of the ether groups very readily. Catechol di-n-amyl ether was found to behave in an exactly similar way, and it became of interest to ascertain whether higher catechol ethers do behave normally in reactions which leave the methoxyl groups of veratrole quite intact. It will be recalled that catechol methylene ethers can be demethylenated fairly readily by certain reagents such as alcoholic potash (Späth and Lang, *Berichte*, 1921, *54*, 3064), concentrated sulphuric acid, or hot dilute sulphuric acid (cf. Tollens, Weber and Clowes, *Annalen*, 1898, *299*, 316 ; *Berichte*, 1899, *32*, 2841 ; Späth and Quietensky, *Berichte*, 1925, *58*, 2267 ; Späth and Holter, *Berichte*, 1927, *60*, 1891). It was, consequently, considered of interest to examine some of the other reactions of catechol di-n-butyl ether and of catechol di-n-amyl ether. The reactions so far examined are sufficiently indicated on the accompanying flow sheet, and it remains only to comment that oxidation of the dihydro anthracene derivative (XIV) with dilute nitric acid (cf. G. M. Robinson, *J.C.S.*, 1915, 267-276) led to some dealkylation, and degeneration of the n-butyl residues. Further, cyclization of the Schiff's base (XV) with concentrated sulphuric acid to the quinoline (XVI) must be carried out in the cold, as even on warming debutylation occurs, as is shown by the separation of oily drops in the acid solution, and the rapid darkening of the organic material in solution when treated with excess alkali and shaken in air. Even when the cyclization with sulphuric acid is carried out at 10° and the solution at once poured on to ice, a strongly minty smell, apparently due to further condensation of extruded



butylene, is noticeable, and it is possible to isolate a phenolic base in addition to the expected quinoline derivative.

The results of further experiments on other higher dialkyl ethers of catechol and on the unsymmetrical alkyl ethers of guaiacol will be reported shortly.

EXPERIMENTAL.

Catechol di-n-butyl ether (1 : 2-Di-n-butyloxy benzene) (I).

This ether has already been prepared by Slotta and Franke (*Berichte*, 1930, *63*B, 686) by butylation of catechol with n-butyl p-toluene sulphonate, and described as a pale yellow oil, boiling at 135-138°/12 mm. or 241-243°/765 mm. In our experiments catechol (55 grams) and n-butyl bromide (150 grams ; excess, more than 2 mols.) were dissolved in absolute ethyl alcohol (250 c.c.) and then under good reflux a concentrated solution of potassium hydroxide (60 grams) in water (40 c.c.) was rapidly run in with good mixing. There was an immediate precipitation of a potassium salt and a violent reaction set in. The potassium salt soon disappeared and then potassium bromide commenced to separate. The mixture was eventually heated under reflux, and after two hours butyl bromide (50 grams) and an equivalent amount of potassium hydroxide solution were added and refluxing continued. After a further two hours the liquid was cooled, mixed with excess of water, and extracted several times with ether. The combined ethereal extracts were well washed with alkali and water, dried and the solvent removed. The residual yellow oil was distilled under reduced pressure, over 100 grams of a perfectly colourless mobile oil boiling at 156-157°/22 mm. being collected.

4-Nitrocatechol-di-n-butyl ether (II).

To a solution of catechol di-n-butyl ether (I) (25 grams) in glacial acetic acid (50 c.c.) was added all at once a solution of nitric acid (D 1·42 ; 15 c.c. ; excess) in glacial acetic acid (25 c.c.). The solution became yellow and heat was evolved, the temperature rising to about 50°. After standing thirty minutes water was added and the precipitated crystalline solid was filtered off and twice recrystallised from ethyl alcohol. It was obtained in long needles only very pale yellow in colour, m.p. 56°. The solid turned brown fairly rapidly on exposure to light. The yield was over 80%.

Found N=5·4% ; calculated for $C_{14}H_{21}O_4N$, N=5·2%.

4 : 5-Dinitro-catechol-di-n-butyl ether (III).

The above desired nitro compound (II) (10 grams) was added to nitric acid (D 1·42 ; 100 grams) in a conical flask, and the mixture gently warmed and stirred. The solid rapidly melted to an oil which deepened in colour to orange. After about 30 minutes the mixture was heated more strongly, when the oil suddenly crystallised, and red fumes developed. Water was added and the precipitated solid was collected and recrystallised from alcohol. It crystallised in magnificent pale yellow micaceous plates, m.p. 124°.

Found N=9·0%; calculated for $C_{14}H_{20}O_6N_2$, N=9·0%.

4-Nitro-5-(N-piperidino)-catechol-di-n-butyl ether (IV).

4 : 5-Dinitro catechol di butyl ether (3 grams) was dissolved in piperidine (6 c.c.) and the mixture very gently refluxed for two hours. The colour commenced to darken at once to orange and after two hours was deep orange-red. It was then poured into dilute acetic acid solution (3 c.c. in 50 c.c.) and the separated red oil was induced to crystallise. It was recrystallised from ethyl alcohol and obtained in magnificent orange-red prisms, m.p. 51°. The yield was approximately 80%.

Found N=8·2%; calculated for $C_{19}H_{30}O_4N_2$, N=8·0%.

This substance was also readily obtained from 4-bromo-5-nitro-catechol di-n-butyl ether by heating with excess of piperidine, and working up the product as above.

4-Bromo catechol-di-n-butyl ether (V).

Catechol di-n-butyl ether (8·3 grams) was dissolved in glacial acetic acid (20 c.c.) and gradually treated with a solution of bromine (2 c.c.) in glacial acetic acid (10 c.c.). Hydrogen bromide was evolved. After standing some time the liquid was diluted and made alkaline and the precipitated oil taken up and dried in ether and finally distilled *in vacuo*, a colourless practically odourless heavy oil (6 grams) boiling at 195-197°/22 mm. being obtained.

Found C=55·3, H=6·7%; calculated for $C_{14}H_{21}O_2Br$, C=55·8, H=7·0%.

4-Bromo-5-nitro catechol-di-n-butyl ether (VI).

4-Bromo catechol-di-n-butyl ether (4 grams) was dissolved in glacial acetic acid (7 c.c.) and a solution of nitric acid (D 1·42; 2 c.c.) in glacial acetic acid (4 c.c.) gradually added with cooling. The liquid darkened in colour, and heat was evolved. After addition of all the nitrating mixture an oil commenced to separate but it crystallised on scratching. Eventually excess of water was added and the solid was collected, washed, and then recrystallised from alcohol. It formed fine pale yellow needles melting at 62°.

Found N=4·4%; calculated for $C_{14}H_{20}O_4NBr$, N=4·1%.

4 : 5-Dibromo catechol-di-n-butyl ether (VII).

A solution of bromine (6·5 grams; 2·2 c.c.) in glacial acetic acid (10 c.c.) was gradually added to a solution of (I) (4·5 grams) in glacial acetic acid (20 c.c.). Hydrogen bromide was evolved. When the colour had been discharged, the mixture was poured into water and the separated oil taken up, washed and dried in ether, and after removal of the solvent fractionated *in vacuo*. A colourless highly refractive oil boiling at 206-208°/23 mm. was collected. The yield was over 80%.

Found C=45·1, H=5·3%; calculated for $C_{14}H_{20}O_2Br_2$, C=44·2, H=5·3%.

4-Amino catechol-di-n-butyl ether (VIII).

Preliminary attempts to reduce the nitro compound II by the method used by Fargher (*J.C.S.*, 1920, 869) for preparation of 4-aminoveratrole, using hot aqueous sodium sulphide solution, were unsuccessful, probably owing to the extreme insolubility of the nitro compound in aqueous solutions. Addition of alcohol to the reaction mixture, so as to bring the reactants into one phase, proved successful, and the method finally adopted was to reflux the nitrodibutyl ether (25 grams) with a solution of crystallised sodium sulphide (75 grams) in water (50 c.c.) and alcohol (150 c.c.) for six hours. The alcohol was then distilled off, more water added, and the oil taken up in ether, washed and the solvent removed. It was then treated with a large volume of hot dilute hydrochloric acid in which most of it dissolved, and after treatment of this solution with charcoal and filtration an excess of sodium hydroxide solution was added. The liberated oil was taken up and dried in ether and distilled *in vacuo*. A colourless oil boiling at 157-158°/1·5 mm. was collected. Yield 80%. The oil rapidly darkened on keeping, even out of contact with air.

Found C=70·5, H=9·8%; calculated for $C_{14}H_{23}O_2N$, C=70·9, H=9·7%.

The *hydrochloride* of this base is but sparingly soluble in cold water, and may be readily recrystallised from hot water. It is thus obtained as a waxy solid, like cotton wool in appearance, m.p. 173°. The aqueous solution froths like a typical soap solution on boiling. The *picrate* is readily prepared by mixing alcoholic solutions of the base and picric acid. It is rather soluble in alcohol and crystallises in yellow plates, m.p. 159°.

4-Acetylamino catechol-di-n-butyl ether (IX).

4-Aminocatechol-di-n-butyl ether (5 grams) was dissolved in dilute acetic acid (15 c.c.) and a slight excess of acetic anhydride added. The acetyl derivative commenced to separate almost immediately and was recrystallised from hot methyl alcohol, from which it could be obtained in fine white needles with a faint pink tinge, or in practically colourless prisms, melting at 97°.

Found N=5·3%; calculated for $C_{16}H_{25}O_3N$, N=5·0%.

4-Acetylamino-5-nitro-catechol-di-n-butyl ether (X).

The above described acetyl compound (XI) (5 grams) was dissolved in glacial acetic acid (15 c.c.) and a slight excess of nitric acid (D 1·42) in an equal volume of glacial acetic acid gradually added, the temperature not being allowed to rise above room temperature. The colour deepened to orange and crystals commenced to separate. Water was added and the crystalline precipitate was filtered off, well washed and then recrystallised from hot ethyl alcohol in which the nitro amide is readily soluble in the hot but only sparingly in the cold, crystallising in fine yellow needles, m.p. 85°.

Found N=8·9%; calculated for $C_{16}H_{24}O_5N_2$, N=8·7%.

4-Amino-5-nitro catechol-di-n-butyl ether (XI).

The nitroamide (X) (3 grams) was dissolved in boiling alcohol (30 c.c.) and concentrated hydrochloric acid (15 c.c.) was added. After refluxing for 30 minutes the alcohol was boiled off and after a further 90 minutes water was added and the precipitated orange crystalline nitroamine collected and recrystallised from hot ethyl alcohol. The yield was practically quantitative. The product crystallised in small orange plates, m.p. 108°.

Found N=10·1%; calculated for $C_{14}H_{22}O_4N_2$, N=9·9%.

4-Acetylamino-5-bromo catechol di-n-butyl ether (XII).

To a solution of the acetylamino compound (IX) (1·7 grams) in glacial acetic acid (10 c.c.) was gradually added a solution of bromine (1 gram) in glacial acetic acid (3 c.c.). The bromine was rapidly decolourised, some heat being evolved, and at the end of the addition the reaction mixture became solid. On addition of water the separated white crystals dissolved and almost at once colourless plates commenced to separate from the faintly pink solution. These were collected and recrystallised from hot aqueous alcohol. This substance is very soluble in alcohol. It melts at 87°.

Found $C=53{\cdot}4$, $H=7{\cdot}0$, $N=3{\cdot}8\%$; calculated for $C_{16}H_{24}O_3NBr$, $C=53{\cdot}6$, $H=6{\cdot}7$, $N=3{\cdot}9\%$.

2 : 3-Di-n-butyloxyphenanthraphenazine (XIII).

(Cf. Jones and Robinson, *J.C.S.*, 1917, 910.)

To a solution of (III) (1·5 grams) in alcohol (30 c.c.) was added concentrated hydrochloric acid (15 c.c.) and then an excess of zinc dust. The solution soon became colourless and when the violent reaction had ceased water (80 c.c.) was added and then to the filtered solution was added a solution prepared by adding saturated sodium acetate solution (15 c.c.) to a solution of phenanthraquinone (3 grams; excess) in saturated sodium bisulphite solution (15 c.c.). The mixture was then boiled. The phenazine precipitated and was recrystallised from an alcohol-dioxane mixture, being obtained in yellow feathery needles, m.p. 190°.

Found $C=79{\cdot}2$, $H=6{\cdot}4\%$; calculated for $C_{28}H_{28}O_2N_2$, $C=79{\cdot}1$, $H=6{\cdot}6\%$.

2 : 3 : 6 : 7-Tetra-n-butyloxy-9 : 10-dihydroanthracene (XIV).

(Cf. G. M. Robinson, *J.C.S.*, 1915, 267-276.)

Catechol di-n-butyl ether (10 grams) was mixed with sulphuric acid (32 grams of 70%), and aqueous formaldehyde (13 grams of 38% aqueous solution) gradually added with vigorous stirring. The oil gradually became more viscous and a dark magenta colour developed. The mixture was eventually allowed to stand overnight and the separated solid was then collected and taken up in hot ethyl alcohol from which a colourless amorphous substance separated on cooling. This was collected and recrystallised from hot absolute alcohol, being thus obtained as a white powder, m.p. 91°.

Found $C=75{\cdot}8$, $H=9{\cdot}7\%$; calculated for $C_{30}H_{44}O_4$, $C=77{\cdot}0$, $H=9{\cdot}4\%$.

Catechol di-n-amyl ether (*1 : 2-Di-n-amyloxybenzene*) (XVII).

A solution of potassium hydroxide (40 grams) in water (20 c.c.) was added in one lot to a solution of catechol (37 grams) and n-amyl chloride (90 grams) in alcohol (150 c.c.). A white precipitate formed, but it redissolved almost immediately. The mixture was then refluxed out of contact with air for four hours, after which amyl chloride (45 grams) was added, followed by a solution of potassium hydroxide (20 grams) in water (10 c.c.). The refluxing was continued for a further four hours. Water was added to the cooled solution and the precipitated oil was taken up in ether, extracted with sodium hydroxide solution, washed with water, dried and distilled *in vacuo.* A colourless liquid (28 grams; 34% of theory) boiling at 174-176°/21 mm. was collected.

4-Nitro catechol-di-n-amyl ether (XVIII).

A solution of nitric acid (D 1·42; 10 c.c.) in glacial acetic acid (8 c.c.) was slowly added to a solution of catechol di-n-amyl ether (10 grams) in glacial acetic acid (20 c.c.), the temperature not being allowed to rise above 30°. The mixture was finally allowed to stand at room temperature during one hour, when crystals of the yellow nitro compound separated. It was then poured on to ice and the precipitated yellow solid was collected and recrystallised from alcohol. Almost colourless needles (9 grams) melting at 49° were obtained.

Found N=4·6%; calculated for $C_{16}H_{25}O_4N$, N=4·7%

4 : 5-Dinitrocatechol-di-n-amyl ether (XIX).

Solution of XVI in nitric acid (D 1·42) in exactly the same way as for III led to formation of the dinitrocatechol-di-amyl ether, which was obtained in bright yellow plates melting at 117° after recrystallisation from alcohol. The odour of amyl alcohol was very apparent during the nitration.

Found N=8·2%; calculated for $C_{16}H_{24}O_6N_2$, N=8·2%.

β-(*3 : 4-Di-n-butyloxyanilino*)-*propenyl methyl ketone* (XV).

4-Aminocatechol-di-n-butyl ether (8 grams) and acetyl acetone (3·5 grams) were mixed and warmed together on the water-bath. Water separated within a few minutes. After standing overnight the oily product was dried in ether and after removal of the solvent distilled *in vacuo*, being thus obtained in almost quantitative yield as a very pale yellow oil boiling at 206-207°/1·5 mm.

Found N=4·6%; calculated for $C_{19}H_{29}O_3N$, N=4·4%.

This substance is much more stable to light and air than the base (VIII), darkening only slowly on exposure to them.

2 : 4-Dimethyl-6 : 7-di-n-butyloxy quinoline (XVI).

The Schiff's base (XV) (3 grams) was slowly added to concentrated sulphuric acid (25 grams) and triturated until it passed into solution, the temperature being kept below 10°. As soon as all was in solution, this was poured on to crushed ice and basified with ammonia. The gummy oil so precipitated, which had a strong smell of sage, was taken up in ether and this solution twice extracted with sodium hydroxide solution to remove phenolic compounds. The alkaline extracts became dark blue very quickly. The ethereal solution was finally washed with water, dried over anhydrous sodium sulphate and the solvent removed. The residual brown oil was distilled under reduced pressure and a pale yellow oil boiling indefinitely between 150° and 180°/22 mm. was collected. This solidified on cooling to a pale yellow solid, m.p. 49°.

Found N=4·7%; calculated for $C_{19}H_{27}O_2N$, N=4·7%.

The combined sodium hydroxide extracts of the ethereal solution above described were acidified with hydrochloric acid and again basified with ammonia. A flaky precipitate was obtained, and after recrystallisation from alcohol almost colourless plates melting at 180° were obtained.

Found C=74·2, H=7·8%; calculated for $C_{15}H_{19}O_2N$, C=73·5, H=7·8%.

This substance thus appears to be a mono butyl ether of 2 : 4-dimethyl—6 : 7-dihydroxy quinoline, one of the n-butyloxy groups having been removed during the reaction with sulphuric acid.

ACKNOWLEDGMENT.

In conclusion, the authors desire to express their grateful thanks to Miss E. Goulston, B.Sc., for some of the analyses recorded in their paper.

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SOME DERIVATIVES OF 6 : 7-DIMETHOXYBENZO-PARATHIAZINE.

By Kenric J. Baldick, B.Sc.,
and Francis Lions, B.Sc., Ph.D.

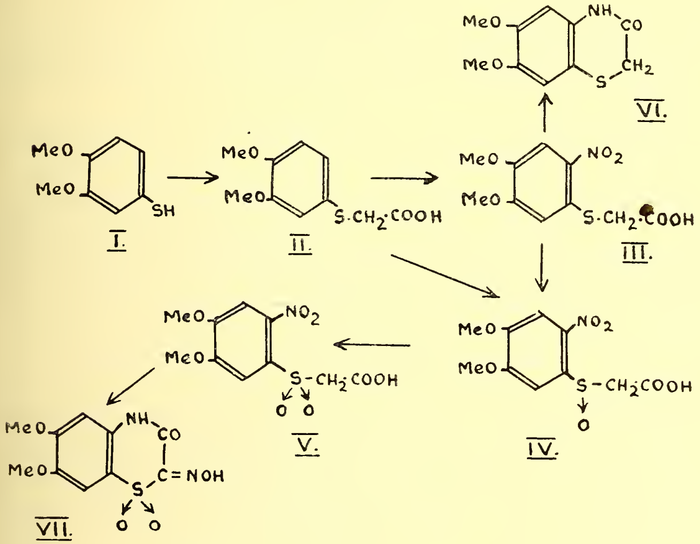
(*Manuscript received, July 21, 1937. Read, August 4, 1937.*)

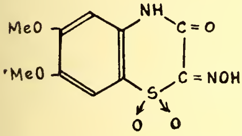
Although the group of dibenzo-para-thiazines—the thiodiphenylamines—is of great importance, and contains such important substances as Lauth's violet and methylene blue, the simpler parathiazine and benzoparathiazine groups are relatively insignificant. The present paper describes the preparation of certain derivatives of 6 : 7-dimethoxybenzoparathiazine. The starting substance was the 1-sulphydryl-3 : 4-dimethoxy benzene (I) described by Fries, Koch and Stukenbroch (*Annalen*, 1929, *469*, 172). Treatment of this in alkaline solution with chloracetic acid leads readily to 3 : 4-dimethoxyphenylthioglycollic acid (II), which on nitration with nitric acid in glacial acetic acid solution at 20° yields 2-nitro-4 : 5-dimethoxyphenylthioglycollic acid (III). Oxidation of III with 3% hydrogen peroxide in acetic acid yields 2-nitro-4 : 5-dimethoxyphenylsulphoxide-acetic acid (IV), which can also be obtained more economically by direct nitration of II with nitric acid in acetic acid at 100°. An attempt to oxidise III to the sulphone with 30% hydrogen peroxide in acetic acid was unsuccessful. However, oxidation of either III or IV with neutral permanganate solution readily yields 2-nitro-4 : 5-dimethoxyphenylsulphone acetic acid (V).

Reduction of III, best with tin and hydrochloric acid, readily yields 3-ketodihydro-6 : 7-dimethoxybenzoparathiazine (VI), a white crystalline substance which melts at 186–187°. Similarly, reduction of V with the same reagents gives 3-keto dihydro-6 : 7-dimethoxybenzoparasulphazone (VII), a white crystalline substance which crystallises with a molecule of water of crystallisation.

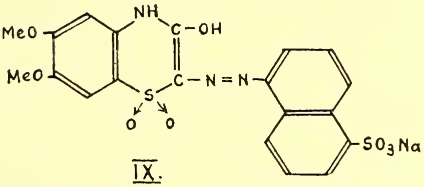
Attempts to condense VI and VII with acenaphthenequinone proved abortive, as did also attempts to condense VII with benzaldehyde under different conditions. How ever, VII reacts with nitrous acid to form the iso-nitroso derivative VIII.

VII also couples with diazotised α-naphthylamine 5-sulphonic acid in sodium hydroxide solution to form a golden-brown azo dyestuff IX.





VIII.



IX.

Experimental.

3 : 4-Dimethoxyphenylthioglycollic acid (*II*).

Veratrole-4-sulphonyl chloride was prepared by the method of Brown and Robinson (*J.C.S.*, 1917, 953) and reduced to I with zinc dust and hydrochloric acid according to the directions of Fries, Koch and Stukenbroch (*loc. cit.*). The thiol (35 grams) was added to a 25 per cent. solution of sodium hydroxide (600 c.c.), when a creamy sodium salt separated, and then was added a solution of sodium chloracetate [from chloracetic acid (35 grams) in water

(35 c.c.) and sufficient solid sodium carbonate for neutralisation]. The mixture was warmed to about 50° and then allowed to stand for two hours. The solid sodium salt soon passed into solution. After filtration the solution was acidified in the cold with concentrated hydrochloric acid, when the free 3 : 4-dimethoxyphenyl thioglycollic acid crystallised in white needles; yield 85%. For analysis the substance was recrystallised from aqueous methyl alcohol and thus obtained in fine white needles melting at 106°.

Found C=52·4, H=4·7%; calculated for $C_{10}H_{12}O_4S$, C=52·6, H=5·3%.

The acid II is insoluble in water, ether, petroleum ether, and cold benzene, but soluble in methyl or ethyl alcohols, acetic acid, chloroform, acetone, and hot benzene. Treated with cold concentrated sulphuric acid it develops a pink colour which becomes olive green on warming.

2-Nitro-4 : 5-dimethoxyphenylthioglycollic acid (*III*).

Concentrated nitric acid (D 1·42; 20 c.c.) was gradually added to a solution of the acid II (20 grams) in glacial acetic acid (80 c.c.), the temperature being maintained at 20°. The solution became red in colour and very soon a thick yellow crystalline precipitate was thrown down. After collection, washing, and recrystallisation from alcohol the solid nitro acid (III) was obtained in yellow matted needles melting at 222°. The yield was 85% of theoretical.

Found C=43·5, H=4·1%; calculated for $C_{10}H_{11}O_6NS$, C=43·9, H=4·0%.

This substance is soluble in hot alcohol, hot acetone and hot acetic acid, sparingly soluble in cold acetone and practically insoluble in cold alcohol, or cold acetic acid. It does not dissolve in water, ether, benzene or chloroform. It dissolves in cold concentrated sulphuric acid giving a blood red colour, which changes to purple on heating.

2-Nitro-4 : 5-dimethoxyphenyl sulphoxide acetic acid (*IV*).

This substance was obtained by two methods.

(*a*) To a solution of the nitro acid (III) (2 grams) in boiling glacial acetic acid (30 c.c.) was added 3% hydrogen peroxide solution (80 c.c.). The yellow precipitate first formed was redissolved after heating for one hour on the water-bath. The clear solution was concentrated by evaporation. On cooling, it deposited a yellow crystalline precipitate (1·7 grams; 80% of theory). Recrystallised from alcohol it was obtained in pale yellow crystalline scales melting at 203°.

Found C=41·6, H=4·0%; calculated for $C_{10}H_{11}O_7NS$, C=41·5, H=3·8%.

(*b*) Concentrated nitric acid (D 1·4; 6 c.c.) was added to a solution of the thioglycollic acid II (4 grams) in hot glacial acetic acid (20 c.c.). A dark red colour developed. The temperature was maintained at about 100° for a few minutes, and then the solution was allowed to cool. A yellow crystalline precipitate (3·7 grams; 73% of theory) separated, which melted at 203° after recrystallisation from alcohol, and was identical with the above described substance.

This acid IV is soluble in acetone, warm acetic acid, and hot alcohol, but is not soluble in water, ether, benzene, chloroform, and cold alcohol. It dissolves in cold concentrated sulphuric acid with production of a yellow colour which changes to brown on warming.

2-Nitro-4 : 5-dimethoxyphenyl sulphone acetic acid (*V*).

The nitro acid III (12 grams) was suspended in a solution of magnesium sulphate (8 grams) in water (400 c.c.) and solid potassium permanganate (10·3 grams) gradually added with stirring, the temperature being maintained at 10–15°. The mixture was finally allowed to stand for one hour, and after removal of the manganese dioxide the excess permanganate was destroyed with oxalic acid. Hydrochloric acid was added to the clear solution, and a white crystalline precipitate (8·5 grams; 64% of theory) was thrown down. Recrystallised from alcohol it formed white scales melting at 200°.

Found C=38·8, H=3·5%; calculated for $C_{10}H_{11}O_8NS$, C=39·4, H=3·6%.

The same acid (2·3 grams) was also readily obtained by a similar neutral permanganate oxidation of the sulphoxide IV (3·7 grams). Attempts to effect oxidation of either III or IV to V using "Perhydrol" in boiling glacial acetic acid as described by Claasz (*Berichte*, 1912, *45*, 747), or under modified conditions, were all unsuccessful, the starting material usually being recovered unchanged.

The acid V is soluble in acetone, hot alcohol and hot acetic acid. With cold concentrated sulphuric acid it gives a yellow coloration which is not changed on heating.

3-Keto-dihydro-6 : 7-dimethoxybenzoparathiazine (*VI*).

Attempts to reduce the nitro acid II with zinc dust and boiling glacial acetic acid (Claasz, *loc. cit.*) gave black unmanageable products. Hence, the following method was elaborated : 2-nitro-4 : 5-dimethoxyphenylthioglycollic acid (III) (5 grams) was mixed with granulated tin (12 grams) and concentrated hydrochloric acid (40 c.c.) added. The mixture was then heated on the water-bath until the yellow nitro compound had completely disappeared. On cooling, white needles separated. Water (200 c.c.) was added and the precipitate collected (3 grams ; 70% of theory) and recrystallised from aqueous alcohol, when it formed fine white matted needles melting at 186–187°.

Found C=53·8, H=4·9% ; calculated for $C_{10}H_{11}ONS$, C=53·3, H=4·9%.

This substance is insoluble in ether, petroleum ether, or cold water, but is sparingly soluble in hot water and soluble in most of the other usual organic solvents. In contact with cold concentrated sulphuric acid it develops a purple colour which deepens on warming.

3-Keto-dihydro-6 : 7-dimethoxybenzo-para-sulphazone (*VII*).

Treatment of the acid V (5·5 grams) with granulated tin (12 grams) and concentrated hydrochloric acid (40 c.c.) on a water-bath led to gradual disappearance of the nitro acid. When all had gone into solution this was cooled and a grey precipitate (4·2 grams ; 90% of theory) separated. It was collected and recrystallised from absolute alcohol and thus obtained in fine white needles melting at 233–234°.

Found C=44·0, H=4·7, N=5·3% ; calculated for $C_{10}H_{11}O_5NS$, C=46·7, H=4·3, N=5·5% ; calculated for $C_{10}H_{11}O_5NS,H_2O$, C=43·7, H=4·5, N=5·1%.

The analytical figures suggest the presence of a molecule of water, and open the possibility of this substance being 2-amino-4 : 5-dimethoxyphenyl sulphone acetic acid. However, on heating the substance in a vacuum desiccator at 110° C. (in the presence of phosphorus pentoxide), its weight decreased by an amount equivalent to the loss of approximately one molecule of water of crystallisation.

0·2446 grams heated at 110°/25 mms. for 3 hours, lost 0·0138 grams. Theoretical loss for one molecule of water of crystallisation=0·0161 gram.

1·0596 grams heated at 110°/25 mms. for 3 hours, lost 0·0610 grams. Theoretical loss for one molecule of water of crystallisation = 0·0690 gram.

Found water = 5·65, 5·78%; calculated for $C_{10}H_{11}O_5NS$, H_2O, water = 6·55%.

The discrepancy between the theoretical loss of moisture and that actually found is almost certainly due to the fact that the anhydrous substance is very hygroscopic, and gained weight rapidly during the operation of weighing.

Further proof of the cyclic character of the compound VII was afforded by the preparation from it of the isonitroso derivative VIII. (Compare D.R.P. 288, 682, Friedlander, Vol. XII, 134.)

The sulphazone VII (1·4 grams) was dissolved in glacial acetic acid (15 c.c.), and 10 c.c. of a solution of sodium nitrite (7 grams) in water (50 c.c.) added. The mixture was filtered and the filtrate allowed to stand in the ice-box overnight.

The yellow solid material (1 gram) which had separated out was filtered off, washed with water, and recrystallised from absolute alcohol (40 c.c.). It formed fine yellow crystals, which decomposed between 195° and 200° C., the exact temperature depending on the rate of heating the bath.

Found C = 42·2, H = 3·7, N = 10·1%; calculated for $C_{10}H_{10}O_6N_2S$, C = 42·0, H = 3·5, N = 9·8%.

Attempts to condense the thiazine VI or the sulphazone VII with acenaphthenequinone according to the method of Bezdzik and Friedlander (*Sitzungsberichte der Akad. der Wiss. Wien*, 1908, *11B*, 117, 146) all failed. Similarly attempts to condense VII with benzaldehyde, using piperidine, sodium ethoxide or hydrogen chloride as condensing agent were all abortive. However, addition of a diazo solution prepared from α-naphthylamine-5-sulphonic acid (1·1 grams) to a solution of the sulphazone VII (1 gram) in sodium hydroxide solution, followed by addition of sodium chloride led to precipitation of the golden brown salt of the dyestuff IX.

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FOR
1937-1938
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PART II (pp. 118 to 622 and pp. i to liii)
OF
VOL. LXXI

Containing Papers read from September, 1937, to April, 1938, and Clarke Memorial Lecture for 1938. With Plates I to XV, also List of Members, Abstract of Proceedings and Index.

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1938

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VOLUME LXXI.

Part II.*

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VOLUME LXXI

PART TWO

THE STRUCTURAL HISTORY OF AUSTRALIA DURING THE PALÆOZOIC.

(THE STABILIZATION OF A CONTINENT.)

By E. C. Andrews.

(With Plate I and seven text-figures.)

(*Manuscript received, August 17, 1937. Read, September 1, 1937.*)

Contents.

General Statement.

Australia itself is a structural unity, being portion of a more complete unity, comprising Australia with its related insular arcs such as New Guinea, the Solomons, New Caledonia, and New Zealand. In continents, such as Europe, Asia, and North with South America, the structural equivalents of these arcs are the Alpine systems, the Tethyan mountain systems, the Asiatic insular arcs, the American Cordillera, and the Andes. For these continents, the unstable areas are, in the main, part and parcel of the continents themselves.

In this note a brief outline is attempted of the history of the Palæozoic seas, lands, and mountains of Australia. At first glance an undertaking such as this may appear simple, but the difficulties become increasingly evident as the work progresses. The difficulties lie rather in synthesis of observations than in analysis. In the first place, a very small portion only of the continent has been surveyed areally; in the second place, ancient borderlands in great measure have disappeared beneath the sea by undulatory earth movements, in Tertiary and post-Tertiary time; in the third place, ancient lands have been concealed under gigantic accumulations of closing and post-Palæozoic sediments within the several great artesian basins of the continent; and, in the fourth place, no definite age can be assigned to many extensive, but apparently unfossiliferous, series of sediments outcropping throughout eastern Queensland, north-eastern New South Wales (Greater New England Province), and the western division of New South Wales (Broken Hill Province).

Among the reports dealing with the structural history of the continent may be noted those of Andrews,[1], Benson,[2] Bryan,[3] Clarke,[4] David,[5] and Jensen.[6]

These reports have been of the greatest assistance in the preparation of the present note, as have also the textbooks of Sussmilch[7] and Howchin.[8] These valuable summaries of New South Wales and South Australian geology respectively should be brought up to date.

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[1] Andrews, E. C., " Structural Relations of Australasia, New Guinea. and New Zealand ", *Jour. Geol.*, 1916, *24*, No. 8, Nov.-Dec., 751-776, " Geographical Distribution of Ore Deposits in Australasia ", *Econ. Geol.*, 1923, *18*, No. 1, Jan.-Feb., 1-25.

[2] Benson, W. N., " Palæozoic and Mesozoic Seas in Australasia ", *Trans. N.Z. Inst.*, 1923, *54*, 1-62.

[3] Bryan, W. H., " Earth Movements in Queensland ", *Proc. Roy. Soc. Queens.*, 1925, 3-82. " Early Palæozoic Earth Movements in Australia ", *Rept. A.N.Z. Ass. Adv. Sci.*, 1932, *21*, 90-92.

[4] Clarke, E. de Courcy, " Pre-Cambrian Succession in....Western Australia ", *Rept. Aust. and N.Z. Ass. Adv. Sci.*, Brisbane, 1930, *20*, 155-192.

[5] David, T. W. E., " A Sketch of..the Geological History of Australia....Tasmania....to the Permo-Carboniferous Period ", *Proc. Linn. Soc. N.S. Wales*, 1894, 541-607. " The Chief Tectonic Lines of Australia ", *Jour. Roy. Soc. N.S. Wales*, 1911, *45*, 1-60. " The Geology of the Commonwealth ", Federal Handbook Brit. Ass. Adv. Sci. (Australia), 1914, 241-290. " Explanatory Notes to the Geological Map of the Commonwealth ", 1-177. Commonwealth Council Sci. and Indust. Research, 1932.

[6] Jensen, H. I., " The Building of Eastern Australia ", *Proc. Roy. Soc. Queensland*, 1911, *23*, 149-198. " Some Geological Features of Northern Australia ", *Proc. Roy. Soc. Queensland*, 1922, *34*, 105-208.

[7] Sussmilch, C. A., " Geology of New South Wales ", Angus & Robertson, Sydney, 1914.

[8] Howchin, W., " Geology of South Australia ", Govt. Printer, Adelaide, 1918.

Other sources of information include the many recent reports on the geology of local areas, particularly those dealing with the Palæozoic structures of Central Australia.

Difficulty again is experienced in the selection of a satisfactory starting point in time. Should a beginning be made with the heroic periods in geology, times apparently, of Titan endeavour, as it were, around which the glow and glamour of extreme antiquity lingers; times when the vast areas of early Pre-Cambrian rocks were undergoing their periods of "Sturm and Drang"; times when, under the heavy blows of circumstance, slowly but surely, they were passing into vast stabilities of paragneisses and intrusive crystallines? Surely, not at such a point, should a beginning be made, for there, metaphorically, one stands on unstable ground, stable though the structures themselves have been for ages; for these results of action undertaken in ancient abyssal laboratories are now so altered by repeated compressive and chemical attack as to need the close attention of an army of skilled field geologists for decades to provide a satisfactory broad classification or correlation of their now widely separated units. Nevertheless, at some earlier period, they appear to have been co-extensive. All that can be said at the present time, with any approximation to reality, is that these nuclei of the existing continent appear to have been formed, step by step, far back in Pre-Cambrian time, by a process of marginal growth, by the addition, or accretion, of mountain chains. These mountain systems are composed, in the main, of rocks which have been subjected to severe compression or folding. In the later Pre-Cambrian, these blocks, once co-extensive as surface features, appear to have been separated by the formation, within them, of structural depressions. A reasonably safe point for the start of our studies, however, appears to be the closing Pre-Cambrian period.

Beginning then, at this stage, it may be shown that the stable block known today as Australia (with Tasmania) has resulted from the welding, or knitting, together of these ancient nuclei. This welding, fusion, or stabilization, took place, almost wholly, during the Palæozoic era.

Australia, as a block which has passed from a series of once separate masses into structural unity, appears to have much in common with the continents of Asia (with Europe), North America, and South America, inasmuch as each consists, in the main, of enormous nuclei which themselves have been stable structures, in the main, since the dawn of the Cambrian at least, these stable masses, in turn, being associated with long belts or zones of former mobility, and which have been rendered stable by strong compressive activities only during some period, or periods, later than the dawn of the Cambrian.

Combining the information available concerning the structúre of Australia by direct information with that which may be inferred legitimately by reason of the similarities which Australia presents to other continental blocks, in which the main structures have been ascertained by actual survey, it may be seen that it is possible to present the main outline of the geological history of Australia with some claim to fidelity since the dawn of the closing Pre-Cambrian era at least.

The old stable surface of Australia, in common again with other continents, is positive in part and negative in part. Its positive portions rise as the shields of south-western Australia, northern Australia, north-eastern Queensland, and Broken Hill. Its negative, or sunken, portions include the Great Australian Artesian Basin, the Desert Basin of north-western Australia, together with the North-west, Perth, and Nullabor Plains Basins. The Murray Basin, in part, probably also is one of these negative stable areas.

Each of these stable blocks is characterised by certain structures, similar to those observed in the ancient nuclei of other continents. The positive blocks, or shields, form low plateaus of outcropping Pre-Cambrian rocks swelling gently from the surrounding plains, and composed, with the modifications noted below, of rock types all intensely compressed and metamorphosed. The negative blocks are covered with rocks either sub-horizontal or of gently undulating attitude, and, generally, Palæozoic, Mesozoic, or Tertiary in age. Sub-horizontally disposed rocks may be present on positive and negative rocks alike. These rock covers, possessing only slight angular values of slope, may be widely distributed in space, although lacking great thickness. Rarely indeed does their aggregate thickness exceed 5,000 to 6,000 feet, even in the deeper portions of the great basins so far as they have been tested. The Great Artesian Basin may be taken as an example of these negative areas ; here the records of very many hundreds of " bores " sunk for water and " oil " reveal a foundation of closely-folded and altered, to highly-altered, rock, whereas the overlying sediments are sub-horizontal and non-metamorphosed, while the greatest depth reached to the foundation is less than 7,000 feet, the general depth of the more pronouncedly basin formation being between 3,000 and 4,000 feet. The relatively thin cover of gently undulating sediments of late Pre-Cambrian, Cambrian and Ordovician age, noted on the Northern Australia Block, illustrates the freedom from marked submergence experienced by the positive areas for vast periods of time.

What a different story, on the other hand, is to be read in the remainder of the continent. If attention, for example, be directed to Eastern Australia, it will be noted that a wide peripheral area there is occupied by a series of plateaus extending from Cape York in the north to the west of Victoria in the south. Tasmania may be included, for this purpose, in Eastern Australia, although now separated by the shallow water of portion of Bass Strait.

These plateaus present several peculiar and instructive features.

In the first place, they appear to be definitely related, as structures, to the associated continental shelf, in that they are wider, and lower in altitude, where they lie opposite to the wider portions of the shelf, while they are narrower, and of greater vertical relief, where they parallel the narrower portions of the shelf.

In the second place, the highest summits of the continent occur within this peripheral zone of highlands (plateaus).

In the third place, they consist, for the greater part, of folded Palæozoic rocks, all the highest plateaus and summits occurring in the area of the strongly folded Palæzoics. In passing, it may be noted that the earlier Australian geologists regarded these highlands as relics of majestic Palæozoic landscapes, resulting from one grand uplift only with subsequent continuous erosion. This belief was engendered by the general appearance of the softened profiles characteristic of the plateaus themselves in areas not trenched with ravines. On the other hand, they may be seen to be the result of repeated re-elevation and erosion of folded rock-masses, their present outlines indicating recent (late and post-Tertiary) considerable elevation, proceeding by stages, of undulatory nature, coupled with concomitant powerful erosion. Their massive fronts reveal the sturdy profiles of youth, as also the profound gorges and valleys which dissect them, and which baffled the skill of the pioneers for many years to make a complete traverse of them.

The romantic and inspiring scenery which haunts the rims and depths of these mountain fastnesses is not the result of mountain decadence and senility, but rather of vigorous and youthful emergence accompanied by powerful erosive attack.

These plateaus then, which occupy the sites of broad zones of compression during the Palæozoic, differ markedly from the vast areas occupied by the highly altered rocks of the older Pre-Cambrian which form the low plateaus, plains, or the basements of the continental platform and related basins. Were the observer to seek the ancient Pre-Cambrian basement of the long belt of the Eastralian and Tasmanian highlands, he would be forced—with the exception of certain long and narrow zones of ancient rocks involved in the Palæozoic compressions and overthrusts—to explore many thousands of feet below the present surface of the compressed sediments of the Palæozoic geosynclines before obtaining traces of them.

In the fourth place, not only are the mountain ranges of eastern Australia and Tasmania confined to this zone of Palæozoic folding, but the area where the Caledonian and Hercynian mountain systems tend to osculate is marked by a lengthy, but relatively narrow, structural depression within which no " folded " mountains outcrop, their places being taken by Permian and Mesozoic rocks of sub-horizontal to undulating attitude, and of non-metamorphosed nature.

In the fifth place, the repeated floodings with basic lavas which Eastern Australia experienced in Tertiary, and post-Tertiary, time (following on a general sinking, or undulatory, movement) were confined to the areas affected by the Caledonian and Hercynian activities.

In the sixth place, there are two belts of modern mountains in Australia, in addition to those enumerated above, and which have strong youthful profiles, but are unaccompanied by Tertiary basic lava floods and buried river gravels. These also occupy the sites of grand Caledonian mountain areas. These are the Macdonnell Ranges of Central Australia and the Flinders Range, with its natural extension, the Mount Lofty Range, in South Australia.

In the seventh place, the Flinders and Macdonnell mountain areas appear to occupy the site of an ancient geosyncline separating the extensive stable blocks of Western and Northern Australia and of the Broken Hill, or Willyama, area. Furthermore, the Eastralian and Tasmanian highlands themselves occupy the sites of two great Palæozoic geosynclines, or earth troughs, arranged within the peripheral portion of the continent, the one extending from Cape York to Newcastle, the other from Sydney to western Victoria, inclusive of Tasmania, being connected thence with the geosynclines of the Mount Lofty, Flinders, and Macdonnell areas mentioned above.

In the eighth place, these geosynclines have histories which differ widely from each other. The sediments of the south-eastern and central examples, which have been raised and compressed strongly, belong to what may be called, in a broad sense, the Caledonian mountain-making period. The Tasman geosyncline, on the other hand, persisted during the Caledonian orogeny in the south and west, and its sediments, in conformable sequence from the Silurian (inclusive) to the close of the lower division of the Carboniferous, were compressed by the Hercynian and Appalachian activities, the while the Caledonian mountain systems had long been stabilized and freed from compression. In this note the Caledonian movements are considered as extending to the close of the Devonian, the Hercynian (with Appalachian) as inclusive of Carboniferous and closing Palæozoic movements.

A study of these broad zones of Palæozoic (and closing Pre-Cambrian) mobility throws a considerable amount of light on the probable extent of the area affected by the Caledonian and Hercynian movements. A superficial glance at the geological map of Australia suggests merely a chaotic assemblage of pre-Cambrian and Palæozoic rocks in all stages of compression and alteration, and it might be inferred thus that little or no information of value would be available for the detection of the areal limits set to Palæozoic foldings in Australia, or for the appreciation of the general appearance of the topography during the Palæozoic era. On the other hand, it is possible to appreciate the broad outlines of the geosynclines during both the main divisions and subdivisions of the Palæozoic. The geosynclines imply a close association with feeding geanticlines, not, necessarily, consisting of very high land, but, nevertheless, possessing vertical relief sufficient, at various stages of a geological period, to produce the enormous loads of sediment accumulated within the neighbouring and sinking troughs. The massive and thick conglomerates and sandstones with shales at one point dying away in thin sheets of more finely-textured material all tell their valuable tales of neighbouring mobile geanticline with distant opposed foreland relatively stable.

When one studies the Ordovician of Victoria, and notes the existence of extremely heavy sedimentations, with only infrequent breaks, over a territory several hundreds of miles in width, the sediments consisting of alternating sandstone and shale or slate, associated in places with arkose and crossbedded materials, and in other places with finely-textured mudstones and slates containing numerous graptolite remains, it seems reasonable to infer that, in the wide area thus affected, there existed a number of geanticlines, arcuate in plan, from which were derived the widespread alternation of sandstone, shale, and other material, while infrequent alongshore silts of great width acted as traps for graptolitic plankton driven ashore by heavy storms.

Each of the main geosynclines considered in this paper appears to have been loaded beyond the strength of its sinking (undulating) foundation; it then was compressed with its load, and thereupon became the site of a geanticline, and there appears to have been a general emergence of other areas in Australia associated with each great local compression. Upon the conversion of the geosynclinal contents into a geanticline, compensation was sought by undulatory movement, in the formation of a sequent geosyncline, or of sequent geosynclines, alongside. The one-time feeding geanticline, at this critical stage, usually became, in part at least, a negative area, while a more active geosyncline may have grown in front of the new, or advancing, geanticline occupying the site, in part or as a whole, of the earlier trough.

Furthermore, studies conducted within the great Palæozoic geosynclinal areas of Australia reveal a decrease of strength in Caledonian and Hercynian compression with progressive passage measured outward from the great feeding geanticlines. This suggests that the folding activities died away among the almost undisturbed sediments, and associated rocks, of the foreland. This fading away of compressive strength as from feeding geanticline to stable foreland, may be noted in many areas affected by the Caledonian and Hercynian activities in the Australian sector. Rarely is a powerful movement of folding of Palæozoic age observed to pass undiminished beneath the undisturbed sediments filling the Great Basins. It is considered, therefore, that the basement of the Great Australian Artesian Basin, together with the basements of the other vast depressions mentioned above, is mainly pre-Cambrian in age.

During the Caledonian movements, the growth of stability in the Australian structure proceeded first as from west to east, thence as from south in an easterly to north-easterly direction. The later, or Hercynian movements, welded the sediments of the Tasman geosyncline and of its sequents on to the great western massif—whose stability had been produced by Caledonian agencies.

It is difficult to make suitable acknowledgments where the writer is indebted to the work of so many others, but special thanks are are due to the authors of the reports and textbooks mentioned above; to Germaine A. Joplin for assistance in the preparation of the Palæogeographic maps and to C. A. Sussmilch for a critical reading of the manuscript.

THE ANCIENT NUCLEI.

These are indicated in Plate I, and they consist of the south-western, northern, and Broken Hill blocks. The name of Yilgarnia, proposed by Cotton,[9] for the south-western mass, is adopted here; the immense northern block may be named Stuartiana, in honour of the intrepid explorer MacDouall Stuart, who first (1862) successfully crossed (and returned across) this vast unknown land clear from south to north. The name of Willyama proposed by Mawson[10] for the ancient rocks composing its main mass may be given to the Broken Hill massif and its former extension west and south.

These are positive elements of the continents, whereas their main negative relatives, co-extensive with them as ancient surfaces, include the Great Australian Artesian Basin, the Desert Basin of Western Australia, and the North-West Basin; to these, tentatively, may be added

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[9] Cotton, L. A., Presidential Address, *Jour. Roy. Soc. N.S. Wales*, 1930, *64*, 50.

[10] "Geological Investigations in the Broken Hill Area", *Memoirs. Roy. Soc. S. Aust.*, 1912, *9*, Pt. 4.

the Murray Basin. The surface of the immense natural feature known as the Great Australian Artesian Basin may be named the Queensland Platform, while the Murray Basin, together with the associated rock outcrops bordering it on the west and north may, with fitness, be named Sturt's[11] Land, in honour of the most heroic and illustrious of the noble band of Australian explorers, and who first (1828–1845), under conditions of incredible difficulties and danger, investigated this vast area and its arid western surroundings.

The great antiquity of Yilgarnia and Stuartiana is indicated by the attitude of their extensive cover of closing Pre-Cambrian sediments, especially over Stuartiana and the northern portion of Yilgarnia. These sediments occur as sub-horizontal, or gently undulating sheets of limestone, quartzite, sandstone, and shale, together with other rock associates. So negligible is the amount of alteration which they have suffered that some of the earlier observers classified them tentatively as unaltered Mesozoic, or even Tertiary, sediments. Superimposed on these late Pre-Cambrian sediments, as patches throughout the great extent of the Northern Block (Stuartiana) are sub-horizontal Cambrian deposits. Ordovician sediments also occur in abundance on these forelands, namely Stuartiana and Yilgarnia. On the outcropping Willyama Block of Mawson, beds of tillite, quartzite, limestones and varves (?) of closing pre-Cambrian age, lie in gentle undulations and with only slight signs of alteration, whereas beyond the actual outcropping mass itself these closing Pre-Cambrian sediments are highly folded and even moderately metamorphosed.

The Pre-Cambrian age of the basement of the Queensland Platform (Great Artesian Basin) is suggested, or indicated, by the distribution of the associated structures. Thus the ancient rocks themselves enclose it to the south-west, west, and north-east, a connecting but sunken ridge of ancient rocks in the north passing apparently from the Cloncurry Region to the Etheridge-Einasleigh area. The Caledonian foldings appear to osculate it near the Macdonnell Ranges on the west, and near the Willyama Block on the east and north-east, while the Hercynian foldings die out against it from the east (the Caledonian foldings not having been observed in that eastern region).

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[11] " Life of Charles Sturt ", Smith, Elder, Lond., 1899, pp. 395.

Moreover, the many hundreds of samples of bore cores from the basement of the Tertiary, Mesozoic, or even Permian sediments in the basin consist of gneisses and metamorphosed sediments. Beyond a mere fringe, therefore, of buried Caledonian mountains in its south-western portion this great negative area appears to be Pre-Palæozoic in age.

The Desert, North-West, Perth, and Nullarbor Basins are filled with sub-horizontal to moderately dipping sediments, beneath which the surfaces of the vast encircling areas of ancient rocks pass gently to form their basements. The foundation of the Murray Basin also consists, probably, of ancient rocks in the main, as suggested by the general sympathy of trend of the surrounding structures with the neighbouring margin of the basin.

Surrounding the Willyama Block, on its eastern extension, various interesting groups of sediments occur, such as unfossiliferous conglomerates, sandstones, quartzites, and shales, all possessing gentle dips and having freedom from metamorphism. These sediments are considered here as early Palæozoic in age, from their structural relations with the associated late Pre-Cambrian types.

The stable remnant of the ancient northern Australian block which was once co-extensive westwards with Stuartiana, but now separated from it by the Great Artesian Basin, may, perhaps, be known as Carpentaria. It comprises the schists and gneisses of the Cape York Peninsula, together with those of the Etheridge, Einasleigh and associated districts. The rocks of this province have an ancient appearance, yet, as a whole, they do not give one the impression of the great age suggested by a study of the shields of Yilgarnia and Stuartina. No Pre-Cambrian, Cambrian, Ordovician or Silurian sediments, sub-horizontally disposed, have been found within the province, as in the shields of Yilgarnia and Stuartiana. Furthermore, not even Devonian or Carboniferous sediments of horizontal attitude have been detected within it. On the other hand, Silurian, Devonian, and Carboniferous sediments occur within its eastern extension, and these have been moderately to strongly folded. So little definite information, however, is possessed about this large region that it is not known whether unaltered or horizontally disposed Middle or Lower Palæozoic sediments may occur within the western extent of Carpentaria, in other words, the area which formed a foreland for Silurian and later activities to the immediate east of Carpentaria.

Bryan,[12] combining his own observations with a summary statement of the work of Ball, Cameron, Daintree, Dunstan, Jack, Jensen, Marks, Morton, Rands, and Reid, states: "If one proceeds south-east from the main Etheridge mass one encounters on the Einasleigh and Copperfield Rivers extremely metamorphosed rocks striking almost meridionally."

He infers that the highly disturbed rocks of the associated Etheridge, Gilbert, and Woolgar areas represent groups younger than those of the Einasleigh and Copperfield areas.

"The metamorphic rocks of the Einasleigh and Copperfield Rivers appear, in the light of the above descriptions, so dissimilar from the typical Etheridge rocks, as described by Ball, that they probably form a distinct and older series, perhaps equivalent to the Cloncurry series, which they closely resemble in intensity of metamorphism and direction of strike....But, both within the Etheridge Goldfield and beyond it, Jensen recognises outliers of a younger series....and which he regards tentatively as of Ordovician age, although he points out that they bear a close resemblance to Pre-Cambrian rocks of the Northern Territory."

In this summary Bryan includes Reid's description of rock types in the Cape River Goldfield which are similar to the metamorphosed series of the Einasleigh and Copperfield areas and of the pre-Devonian "mica, andalusite, and chlorite schists" of the Charters Towers area.

Bryan's notes suggest also that the "gneisses and schists" of the Chillagoe, Dargalong, Coen, Hamilton, Carbine, and some other areas of Carpentaria are representatives of ancient rock systems.

These descriptions of the rock groups of Carpentaria recall, in some manner, the peculiar rock occurrences of the Willyama (Broken Hill) region, where ancient Pre-Cambrian paragneisses and orthogneisses (though possibly not so ancient as the oldest of the Yilgarnia and Stuartiana rocks) are associated with upper, or closing, Pre-Cambrian sediments, together with other unfossiliferous, but younger sediments referable, probably, to the early Palæozoic.

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[12] Bryan, W. H., "Earth Movements in Queensland", *Proc. Roy. Soc. Queensland*, 1925, *37*, 8-11.

Bryan also, in the same report, discusses the nature of various long belts, or zones, of highly folded and altered rocks lying to the south of Carpentaria, which are arranged *en echelon* within the more eastern portions of Queensland. Among the more important of these may be mentioned Dunk Island, Barnard Island, the wide belt extending sub-meridionally through Mt. Coolon, that also through Clermont, Anakie, and still farther south, together with the Gladstone area. Of these the Clermont-Mount Coolon belt (or belts) is described by the Queensland geologists as slate, mica-schist, hornblende schist, quartzite, and other altered types, overlain unconformably by Devonian limestone (p. 11).

The rock exposures of the Gladstone area are described as an older series of "very highly metamorphosed and crushed schists and gneisses" of ancient appearance and presenting marked differences in strike and lithology from the associated representatives of the Brisbane Schist Series :

"The most metamorphosed series of these old rocks of the Gladstone district is a belt of highly contorted schists and gneisses which probably underlie, or are basal to, the slates of the turquoise belt."[13]

On the assumption that the turquoise belt "is the lowest 'zone' of the Brisbane Schists as typically developed, and as it is supposed (though not on conclusive evidence), to be of Ordovician age, the Gatcombe Head series may be, and probably is, of great antiquity".[14]

Again, marked divergences of opinion appear to be held concerning the age of the rocks composing the D'Aguilar Range (Brisbane Schist Series) and those occurring in various portions of the Burnett River drainage, whether Pre-Cambrian in part, or whether possible wholly Palæozoic.

The folded and altered rocks comprising the slates, sandstones, and conglomerates of eastern New England, and the associated rock belts of altered appearance, lying north-easterly of these, in New South Wales, are, probably, southerly extensions of certain folded and altered forms occurring in south-eastern Queensland.

Bryan[15] concludes that the Einasleigh and Copperfield areas are Pre-Cambrian ; that the Gilbert, Woolgar, Cape

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[13] Jensen, H. I., quoted from Bryan, *ibid.*, p. 11.

[14] Bryan, W. H., *ibid.*, p. 12.

[15] *Ibid.*, pp. 14-15.

River and Charters Towers metamorphism may be due to Pre-Cambrian, but more probably to epi-Ordovician, activities, and that " in Central Queensland there occur a number of old formations of different lithological types which have all been folded on north-easterly axes. In most cases this folding may be reasonably considered as possibly Pre-Ordovician and, probably, pre-Silurian ".

H. C. Richards[16] considers that these belts of altered rocks in eastern Queensland, south of lat. 15° S., are very old, the Dunk Island, Gatcombe Head (Gladstone) types being, possibly, Pre-Cambrian, while the Brisbane Schist types, although younger, are still old. It is, as Richards points out, a peculiar fact—on the assumption that these rocks are of Palæozoic age—that, in spite of diligent search among them by competent observers, they have yielded no recognizable organic forms to date, whereas, on the other hand, strongly folded and definitely altered rocks in New South Wales and Victoria have yielded an abundance of organic remains. It is proposed, in this note, to regard the Gatcombe Head, Dunk Island, Clermont, and a few other types as Pre-Cambrian, and others, such as the Brisbane Schist Series, as younger, but somewhat comparable in age. It may be advisable, however, to note that Devonian rocks, closely folded, occur at no very great distance from exposures of the Brisbane Schist Series.

The mass of slate and associated rocks which contains the principal gold-bearing areas of eastern New England has been referred, generally, to the Silurian, or, at least, to Pre-Devonian time. At various times it appears to have supplied the sediments of the troughs lying west and east of it. It may, perhaps, be known as Ancestral New England, and, for the purpose of this note, its age may be taken as Pre-Devonian.

THE UPPER PRE-CAMBRIAN PERIOD.

The various exposures of sediments in Australia usually referred to the Upper Pre-Cambrian period are known as the Elvire Series in the north-west, or Kimberley district, the Nullagine Series in the central and western portions of Western Australia, the Pertaknurra and Pertatataka in the Macdonnell Ranges, the Flinders and Adelaidean in South Australia, and the Torrowangee or Poolamacca in north-western New South Wales. It is not known which,

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[16] Personal communication, 1937.

if any, portion of the ancient rocks of Queensland, Victoria, or Tasmania are referable to the Upper Pre-Cambrian.

The Nullagine sediments cover "an area exceeding 300,000 square miles",[17] and the depression in which they were deposited must have occupied a much larger area still of Australia.

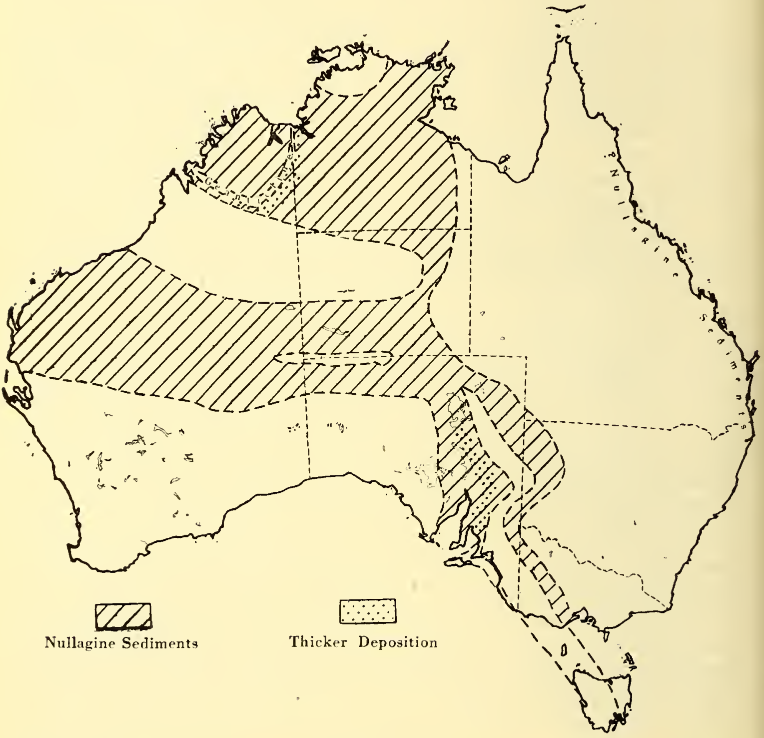

Fig. 1.—Upper Pre-Cambrian. Much of the sedimentation may have been terrestrial.

In the absence of fossil evidence, it is customary to place these sediments in the closing Pre-Cambrian. This is suggested by their attitude of general conformability with the overlying Cambrian (wherever Cambrian sediments are associated with them), and by their general lithology and

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[17] David, T. W. E., "Explanatory Notes", 1932, p. 33, Commonwealth Council Sci. and Indust. Research.

lack of metamorphism as contrasted with the associated Pre-Cambrian, upon which they lie, in many places, with sub-horizontal attitude and with lack of metamorphism. David[18] and Tillyard consider the Adelaidean Series to contain remarkable assemblages of marine life, especially in the quartzitic members of the group, but an examination of David's collections, now housed at Sydney University, suggests that much better preserved material must be obtained before an organic origin can be ascribed, with reason, to the forms described. The sediments of this group are considered by some authorities to be of marine origin, although the greater portion probably had a terrestrial origin.

Sediments and associated volcanics of this age occur mainly as relatively thin sheets over the enormous forelands of Yilgarnia and Stuartiana. The thicker portions of the deposits, however, were laid down in ancient geosynclines. The grander examples of these include :

1. The Elvire Series.

Consisting of quartzites, grits, conglomerates, shales, dolomitic limestones, capped by basalts. The basalts in places are 3,000 feet in thickness. These sediments lie in a great curved area whose convexity is directed southwards towards Yilgarnia and south-easterly to easterly towards Stuartiana. The estimated thickness of the sediments in the Elvire section is from 8,000 to 15,000 feet. They lie with marked unconformity upon the ancient gneisses of Stuartiana, and they are described by Wade[19] as belonging to the Lower Cambrian, or possibly the Upper Pre-Cambrian.

2. The Nullagine Series.

These sediments occur on the northern margin of Yilgarnia and consist of coarse conglomerates, succeeded by glauconitic sandstones, basic to acid lavas, shales, limestones, and quartzites.

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[18] David, T. W. E., and Tillyard, R. J., " Explanatory Notes ", 1932, p. 35, Memoir on Fossils of the Late Pre-Cambrian (Newer Proterozoic) from the Adelaide Series, S. Australia. Angus & Robertson, Sydney, 1936.

[19] Wade, A., " Petroleum Prospects—Kimberley District ", Commonwealth of Australia, 1924, 9-10.

3. The Pertatataka Series.

This series consists, according to Madigan,[20] of basal conglomerates and quartzites (1,000 feet), succeeded by "green micaceous flags, calcareous slates, quartzites, oolitic limestones and red sandstones and purple slates, to a total thickness of more than 2,000 feet". Madigan notes that the Pertatataka beds pass upward conformably, apparently, into the Cambrian, by means of red passage beds "making a remarkable parallel with the Adelaide series, where red beds, the purple slate series, usher in the Archæocyathinæ limestones, as is the case in Central Australia". These sediments were deposited in a geosyncline whose basement consists of the ancient Pre-Cambrian rocks of Stuartiana, the Pertatataka not lying directly upon these, but upon the Pertaknurra, which Madigan suggests may be coeval with the Mosquito of Western Australia, which lie unconformably upon the gneisses of Yilgarnia, and are overlain unconformably in turn by the Nullagine. So also in the Macdonnell Ranges the Pertaknurra is a formation of massive quartzite, limestone, red, chocolate, and calcareous shales, about 3,400 feet in thickness, lying with pronounced unconformity upon the ancient basement (Arunta Complex), and all, in places, highly folded, crumpled, and metamorphosed.

Although the Pertatataka Series overlies the Pertaknurra, apparently conformably, Madigan reports the occurrence of fragments or boulders of the Pertaknurra in the basal conglomerate of the Pertatataka. A consideration, however, of Madigan's published sections suggests the question "Is it possible that the Pertaknurra and the Pertatataka are really one continuous sequence of sediments, the lower, or more northerly members of which have been more severely compressed (and intruded) than the higher members, by Caledonian activities, with consequent overthrusting southwards, thus involving themselves with beds of the same period higher in the sequence"?

The geanticline which fed the Pertatataka appears to have existed as a series of mobile mountain ranges to the north, arranged sub-parallel with the Macdonnell trough. These ranges appear to have been rejuvenated from time to time, the southern mass of Yilgarnia being a foreland. The Queensland Platform and the southern portion of

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[20] Madigan, C. T., "The Geology of the Macdonnell Ranges. . . .", *Rept. Aust. N.Z. Ass. Adv. Sci.*, Sydney, 1932, *21*, 78.

Stuartiana, in part, appear also to have acted as forelands for the eastern and north-eastern portions of the Macdonnell sedimentation. Against these the much later Caledonian thrusts were directed, but especially towards the south. The welding together of Yilgarnia and Stuartiana by Caledonian movements is considered later.

4. The Flinders and Adelaidean Series.

The sediments of the Adelaide Series have a great development in the Adelaide district and they are probably as much as 13,000 feet in thickness. Howchin has accomplished pioneer work in his analysis of the nature of these rocks, and H. Y. L. Brown has shown their great and peculiar distribution and structure throughout South Australia. In ascending succession they consist of conglomerate, grit, limestone, quartzite and " clay-slate ", tillite (1,500 feet), dolomite, slate, limestone, purple slate, and quartzite. The sediments of the Flinders Range, stretching far to the north of Adelaide, are similar to the Adelaidean Series, but with the addition of basic lava flows somewhat similar to those of Kimberley. These sediments were deposited in a geosyncline arranged sub-meridionally and bordered by the ancient mass of Yilgarnia to the west, and that of Willyama to the east. This structural trough was probably connected with the east-and-west Macdonnell trough of Central Australia by means of shallow marine flooding of an area now concealed beneath the sub-horizontal sediments of the Australian Platform. Yilgarnia appears to have been the foreland over whose eastern margin the Adelaidean sediments thinly overlapped, while the feeding geanticline appears to have been situated to the east, forming a portion, if not the whole of Willyama, which extended, in all probability, far to the south of the present limits of that ancient land mass.

5. The Torrowangee Series.

The Torrowangee, or Poolamacca, sediments of Willyama (Broken Hill District), which were described in 1912 by Mawson,[21] consist of quartzite, conglomerate, shale, tillite, dolomite, and basic lavas.

The existence of definite Upper Pre-Cambrian sediments in Tasmania, Victoria, and Queensland is not known.

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[21] " Geological Investigations in the Broken Hill Area ", *Memoirs Roy. Soc. S. Aust.*, 1912, *2*, Pt. 4.

Certain altered sediments, however, in these States, appear to be Pre-Cambrian, and some of them may well be Upper Pre-Cambrian.

CAMBRIAN.

At the very beginning of definite Cambrian time in Australia, one may note the great shrinkage in area of the down-warped structures which had received the Upper Pre-Cambrian sediments. A definite elevation of a vast extent of the more western portions of Western Australia at this time marked one of the earliest stages known in the gradual stabilization of the Australian continent, as from west to east.

As Whitehouse[22] notes " . . . it is not easy to delimit the Cambrian in Australia. Trilobite faunas are first known in the Cordilleran region of North America (*Nevada* Stage). The earliest Cambrian beds in the Atlantic Province have no trilobites either in Europe or in North America. Preservable trilobite faunas would seem not to have reached that region until later in the Lower Cambrian (*Holmia* Stage). In the province represented by Asia and Australia, which, faunally, is a unit in the earlier, though not in the later parts of the period, the appearance of such faunas was even further delayed and no trilobite faunas are known earlier than the *Protolenus* Stage although appropriate lower beds, suitable for preserving fossils, occur."

" In Australia we do find earlier, although non-trilobite faunas. The most important of these are the Archæocyathinæ."

Whitehouse notes also that an additional " difficulty is the disagreement between various workers in other lands about the top of the Cambrian ".

The Lower Cambrian sea in north-western Australia appears to have opened to the ocean only in the Kimberley region, and Lower Cambrian sediments in that area are reported to lie unconformably on the Antrim Plateau basalts (Upper Pre-Cambrian). In the Macdonnell area and in South Australia they are separated from the Pre-Cambrian sediments proper by a vast thickness of red or purple beds (8,000 feet thick, approximately) in the Adelaidean Series. These beds may be of the nature of a passage series. Sedimentation continued during the Lower

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[22] " Cambrian Faunas of North-eastern Australia ", *Mem. Queensland Museum*, 1936, *11*, 70.

Cambrian in the Kimberley, Macdonnell, Flinders and Adelaide geosynclines, while with this was associated extensive shallow flooding of the ancient forelands. The areas so submerged, however, were much smaller than those which had been covered during the preceding period (Upper Pre-Cambrian).

Fig. 2.—Cambrian Seas.

The sub-horizontal beds of Lower Cambrian age overlying the forelands consist of limestones, sandstones, cherts and shales, whereas the thick sediments of the geosynclines consist of massive limestones, quartzites, sandstones and shales. The faunal stages of this division of the Cambrian may be taken as *Salterella*, *Archæocyathinæ*, *Protolenus*, and *Redlichia*.

The Middle Cambrian was marked by further shrinkage of marine conditions from north-western Australia, but with shallow flooding still over Northern Australia. The geosyncline at Kimberley appears to have vanished in great measure, but the geosyncline of the Macdonnell area was still open, although apparently more restricted in width than it had been during Pertatataka time.

Following Whitehouse, in his faunal determinations, the Adelaide geosyncline would appear to have persisted for a very brief period of the Middle Cambrian, but an emergence of this area appears to have checked sedimentation there at an early stage in the Middle Cambrian. The close folding and marked alteration of these Lower and Middle Cambrian sediments may have taken place at this stage, but possibly they are referable to a somewhat later stage of the Caledonian movement, as will be considered later.

In the Middle Cambrian, a definite migration eastward of the continental sea from the Adelaide geosyncline is indicated. Victoria, and probably also New South Wales, were visited for the first time in the Palæozoic by the Middle Cambrian sea. Continuity of marine conditions was established probably between the Victorian sea and the shallow flooding of Northern Australia by way of New South Wales and Willyama. Whitehouse shows that the trilobite types characteristic of Northern Australia and of Victoria are *Dinesus*, *Amphoton*, and *Anomocare* (? Victoria). The sediments of this age in Victoria are finely-textured mudstones, limestones, shales, cherts, with diabases and ash beds in places ; they outcrop usually on the cores of structural belts and they are closely folded and have suffered much from overthrusting and other faulting.

Upper Cambrian sediments occur in Northern Australia and are reported also from Tasmania. The shallow flooding of northern or north-eastern Australia, which had been so marked a feature in Lower and Middle Cambrian, was continued during the Upper Cambrian, but only over a more restricted area. Geosynclinal deposition, within the main continental area, appears to have been checked in great measure.

" With a few exceptions, it is impossible, with the present state of knowledge in Tasmania, to assign any definite age to the Lower Palæozoic rocks which occur between the Pre-Cambrian schists and the West Coast Range Conglomerate series, which is, with a reasonable degree of accuracy, regarded as forming the base of the Silurian system. For this reason, the rocks of the . . . two systems

(Cambrian and Ordovician) are generally referred to as belonging to the dual system—the Cambro-Ordovician."[23]

Nye mentions sediments of definite Cambrian age as occurring at Caroline Creek (sandstones), the Florentine Valley (slates), and the Arthur River (slates). These all are from the western portion of Tasmania. Whitehouse refers these Tasmanian occurrences to the Ozarkian, with *Asaphellus* types of trilobites. He reports that he has not had access to the fossil collections from the Kimberley District and from the Dolodrook limestone of Victoria, but that a study of all the material available to him indicates that Tasmania was the only portion of Australia subjected to marine invasion during Ozarkian time. Kobayashi,[24] however, suggests that these Tasmanian forms may be earliest Ordovician.

No definite occurrences of Cambrian sediments are known from New South Wales, although certain of the Broken Hill sediments, such as the Mootwingee and Nundooka conglomerates, quartzites, sandstones, and shales, as also certain altered sediments of the Bogan and Greater Cobar districts may well belong to the very early divisions of the Palæozoic. Ida A. Brown[25] made important contributions to our knowledge of the Palæozoic in south-eastern New South Wales. In the paper cited she has suggested a possible Cambrian age for certain sediments in the southern portion of the coastal area of the State because (1) they " consist of a series of black-banded, radiolarian cherts and metamorphosed fine-grained sediments now converted into phyllites and schists " ; (2) they, apparently, present great lithological differences from the known Upper Ordovician sediments of the area : (3) they appear to be markedly similar to the recorded Cambrian sediments of Victoria ; (4) their arrangement suggests a possible unconformity between them and the neighbouring Upper Ordovician sediments.

While awaiting confirmatory evidence of this statement, the Cambrian Sea is not indicated, on the accompanying Fig. 2 as extending eastward to the New South Wales coast, for the facts must not be overlooked that our present

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[23] Nye, P. B., personal communication, 1925.

[24] Kobayashi, T., " Notes on Some Ordovician Faunas of Tasmania ", *Jour. Geol. and Geog., Nat. Res. Council*, Japan, 1936, *13*, Nos. 1 and 2, 178-181.

[25] " Geology of the South Coast of New South Wales ", *Proc. Linn. Soc. N.S. Wales*, 1933, *58*, 335.

knowledge suggests that the Ordovician follows conformably on the Cambrian in Victoria, Central, and Northern Australia ; the lithology of the Cambrian varies markedly in the various States ; Ordovician sediments within the various States differ remarkably also among themselves, lithologically ; moreover, competent and incompetent beds respond differentially to compression. It is felt that Cambrian sediments do occur in New South Wales, but the confirmation of such belief must be decided either on fossil evidence, on connected areal survey, or on undeniable structural and lithological relationships. Australian geology, it may be noted, presents scores of similar problems dealing with Upper Pre-Cambrian and Lower Palæozoic time. Especially is this statement true of the more coastal areas of Eastern Australia, from the southern portion of New England to Cape York.

A single example taken from the coastal area of north-eastern New South Wales will serve to illustrate the difficulties encountered in field work. Kenny[26] states that the Nambucca Series consists of finely-bedded sandstones and sandy shales with argillaceous sediments, phyllitic in places and closely folded. The general strike is east and west, but the structure of which it forms a part is complex and dominantly synclinal, with an undulatory pitch northwards at low angles. The Fitzroy Series lies a little distance to the north of the Nambucca Series, forming a broadly sympathetic structure with that of the latter, dipping northerly, but with consistently high dips. Claystones and grits, largely tuffaceous, with conglomerates in places, form the main portion of the sediments, but " intrusive tuffs " occur also, especially in the lower portion of the section. The Nambucca and Fitzroy Series, according to Kenny, are the equivalents of the Brisbane Schists of south-eastern Queensland. Both are, apparently, unfossiliferous. Their age is unknown, but Voisey[27] assigns, provisionally, to the Nambucca Series an Ordovician age, and to the Coffs Harbour Series (Fitzroy of Kenny) a Silurian age.

Although there is no known occurence of unconformability between Cambrian and Lower Ordovician sediments in Australia, nevertheless there were broad emergences

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[26] Kenny, E. J., *Annual Report Dept. Mines, N.S. Wales*, 1935, p. 85.

[27] Voisey, A. H., " A Preliminary Account of the Geology of the Middle North Coast District of New South Wales ", *Proc. Linn. Soc. N.S. Wales*, 1934, *59*, 333-347.

both during the Cambrian and at its close, which tended to increase the growing stability of the continent in a general direction as from west to east, and which caused the Palæozoic seas, moreover, to migrate, in a general way, from the west towards the east.

The Ordovician.

The emergence at the north-western end of the Nullagine (Upper Pre-Cambrian) continental depression had continued throughout Lower, Middle and Upper Cambrian time, and at the opening of Ordovician time the continental sea extended but little northwards of the Tropic of Capricorn.

The area which had been shallow-flooded during the Cambrian in northern Australia by this time had shrunk very considerably also, and its thin sediments, like those of its associates, the Cambrian and Nullagine, on the great foreland of Stuartiana, still lie sub-horizontally, or with gentle undulations only.

The grand Macdonnell geosyncline was still in the mobile stage and Ordovician sedimentation followed conformably on the Cambrian until 6,000 feet of deposits, approximately, had been accumulated therein. The sea here appears to have been shallow, and the great thickness of sediments laid down consist mainly of sandstone and quartzite " with thin and highly fossiliferous bands of limestone near the middle of the series ", according to Madigan. The fossils consist, mainly, of *Orthis leviensis*, *Isoarca*, *Raphistoma*, with large and abundant cephalopods. The sediments of this age were named the Larapintine many years ago by Ralph Tate ; they possess high dips along their northern development, while the folds appear to fade out to sub-horizontality over the southern foreland of Yilgarnia.

The source of these sediments appears to have been an east-and-west range lying immediately to the north of the present Macdonnell Range area, and this range, or geanticline, appears to have been revived continuously through the Pertaknurra-Pertatataka (Nullagine), the Pertaoorrta (Cambrian), the Larapintine (Ordovician), and the Pertnjara (? Silurian).

The extensive Ordovician exposures of the Macdonnell area do not appear to have been divided, as yet, into Lower and Upper, and they are treated as one group in this note.

Great changes in the topography, however, had been taking place in south-eastern (and probably also in eastern)

Australia, and it is here that the Ordovician admits, in places, of division into a Lower and Upper Series.

It would seem probable from the distribution of *Raphistoma* and the cephalopods that there existed a connection between the Ordovician of Tasmania, Victoria, and the Macdonnell trough. The most likely line of connection was by way of Lake Eyre, the margin of Willyama, thence bending towards western Victoria and beyond that State into Tasmania. Such connection, if existent, is now concealed beneath the cover of Mesozoic and Tertiary sediments of the western portion of the Queensland Platform (Great Artesian Basin).

Geologists working in Tasmania have experienced great difficulty in attempting to separate Cambrian from Ordovician sediments; and the great mass of sediments of Lower Palæozoic age which cover most of Tasmania, with the exception of the Pre-Cambrian rocks of the western area, are classed officially as Cambro-Ordovician.

The Lower Ordovician in Victoria overlies the Cambrian conformably "from which it is separated by the incoming of the graptolites. The subdivisions of the Ordovician are based on graptolite zones. No breaks are recorded in the system."[28] The main subdivisions consist of the Lancefieldian (5,000 feet), the Bendigonian (1,500 feet), the Castlemainian (1,000 feet), and the Lower and Upper Darriwilian (3,200 feet). Thomas points out that the lithology of the Lower Ordovician rocks in Victoria "is very constant, consisting of mudstones, shales, slates, sandstones, and grits".[29] They are "very closely and sharply folded along N.S. axes, and complicated by faulting".

The main development of the Lower Ordovician rocks in Victoria lies west of the meridian of Melbourne. Here the closely folded sediments of this age extend almost unbrokenly over an extent of country (save for various overlying, and very gently folded, Devonian and "Carboniferous", with sub-horizontal Cainozoic rocks) having a maximum width of two hundred and fifty miles, and a maximum length, along the strike, of two hundred miles. Eastwards of the meridian of Melbourne, Lower Ordovician rocks in Victoria occur only in isolated patches,

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[28] Thomas, D. E., Handbook for Victoria. Aus. and N.Z. Ass. Adv. Sci., Melbourne Meeting, 1935, p. 96.

[29] *Ibid.*, p. 101.

as in the Mornington Peninsula; at Boolarra; in the Mansfield district; the Howqua River; and at the Myrtleford and Gibbo Creek districts, in north-eastern Victoria. With the exception, however, of the important exposure at Mornington Peninsula (south of Melbourne) the recorded outcrops to the east are small, and not at all representative as are the massive exposures to the west.

There is one doubtful record of Lower Ordovician from New South Wales, but the fossil specimen on which the record was based is considered generally to have been unsatisfactory. The specimen, moreover, appears to have been lost.

The strike of the Lower Ordovician rocks in the area west of Melbourne is curved, but possesses a general meridional direction, the beds plunging in converging folds beneath the Cainozoic beds of the Murray Basin. A study of the geological map of Eastern Australia, however, suggests a curving trend for the Lower Palæozoic rocks in New South Wales, those in the eastern portion of the State possessing a general northerly to north-north-westerly direction, while the Upper Pre-Cambrian to Lower Palæozoic sediments in the western portion appear to have been moulded against the ancient mass of Willyama, being bent towards the west as they are traced north from Victoria, thence almost easterly as they pass to the south of Broken Hill, and thence with a north-north-west to north-westerly strike to the north of Broken Hill, preparatory to plunging under the Mesozoic and Cainozoic cover of the Queensland Platform. This may explain the apparent absence of the continuation of the western Victorian Lower Ordovician in New South Wales, but it does not explain the apparent discontinuity of the few eastern Victorian occurrences when followed northwards towards New South Wales. The rocks described by Ida Brown, and noted above, merely offer an example of the difficulties experienced throughout the whole of Eastern Australia in attempting to assign definite ages for the various groups of non-fossiliferous closely folded and altered rocks encountered in ordinary field work during mining surveys. In this connection it may, perhaps, be not out of place to anticipate somewhat at this stage by stating the difficulties experienced by Victorian geologists in attempting to assign an age to the Mitta Mitta Series of metamorphics in eastern Victoria. At one stage these rocks were classed officially as Silurian (Ordovician); at a later stage as Archæan, by reason of their intense alteration, whereas they have now been shown to be mainly Upper Ordovician. Again, other sediments in New South Wales, thought to be of great antiquity, have been shown, in recent years, to be no older than Upper Ordovician and Upper Silurian, whereas others considered as Silurian have been found to be early Pre-Cambrian. At this stage it may be sufficient to state that, in all probability, Lower Ordovician rocks do outcrop in New South Wales.

No rocks known definitely to be Ordovician have been recorded from eastern Queensland, but the consideration of this is reserved for the general discussion on the Upper Ordovician problem in Australia.

The distribution of the Lower Ordovician in Victoria presents an interesting problem in ancient topography. The area over which folded sediments of this age occur in the State is about four hundred miles in width, the sediments being almost continuous (across the strike) throughout the western two hundred and fifty miles, the outcrops being rare and small in the east.

Thomas,[30] summarizing the Victorian work in the light of his own extensive and original field research, states that the Lower Ordovician is conformable with the Cambrian, but that the boundary is associated with the incoming of sandstones (and graptolites):

" The rocks of the Ordovician are similar, wherever found, in the State. They point to rapid epicyclic changes, sandstones (and even arkoses), grits, mudstones and shales, the latter being the fossiliferous graptolite shales. In the sandstones, apart from one record of fragments of shells, no fossils occur ; in the shales, phyllocarids, graptolites....

" There is no locality where preponderance of grits or sandstones is marked, or even regions where there are thick mudstones. The beds are generally thin, sandstones sometimes twenty to thirty feet thick, and mudstone belts....sometimes may be fifty feet thick.... In these mudstone belts only a small thickness as a rule is graptolitic.... "

According to Thomas the deposition was " certainly away from land " as the fossils are of " deep water aspect ", and occur only in the finer bands.

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[30] Private communication, 1937.

David[31] states that :

"The large area of eastern Australia, lying generally to the east of this old shoreline (that is, the Glenelg region, in general, in western Victoria) appears to have been a relatively deep sea. In Victoria there is a great development of Ordovician rocks of a pelagic graptolitic type belonging to this sea."

A geanticline is indeed indicated as existing during Lower Ordovician time on the eastern portion of Willyama and on its continuation southwards through eastern South Australia, western Victoria, and Tasmania, but the remarkable sedimentary record noted by Thomas cannot well be explained as being the sole product of one great western geanticline, yielding an alternation of sandstones, shales, and mudstones in a deep sea four hundred miles, or more, in width, the sediments being accumulated therein to a thickness exceeding 10,000 feet.

Thomas, as stated above, points out that "in these mudstones only a small thickness, as a rule, is graptolitic ". It would therefore, perhaps, be helpful to picture the Victorian area, in Lower Ordovician time, not as a wide deep sea with a mere fringing geanticline on the west, but rather to see it as a region in which long insular arcs, possibly of low to moderate relief, mobile in character, alternated with meridional seas, or troughs, containing deep water in places, the tendency being for marine conditions to predominate in the western area, and for land to be more prominently developed in the eastern portion of the State. Moreover the graptolite shales suggest the existence of extensive silt flats adjoining the lands, with storms driving the planktonic graptolites onshore to be trapped and preserved in the silts.

In view of the fact that no unconformity has been observed between the Cambrian and the Ordovician, it would appear that no strong compressive activity in the Caledonian period has occurred within Australia up to the close of the Lower Ordovician, with unlikely exceptions within north-western Australia and the Flinders-Adelaidean region in South Australia. Great emergences had taken place, however, in various places such as western New South Wales, Victoria, and Tasmania.

In the succeeding stage, namely the Upper Ordovician, the geographic history is still somewhat indistinct ;

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[31] "Explanatory Notes ", 1932, pp. 39-40.

nevertheless it is more easily interpreted than the Lower Ordovician and the Cambrian.

It has been pointed out already that the Lower and Upper Ordovician have been treated together in the Macdonnell area, in Northern Australia, far-western Queensland, and in Tasmania. Upper Ordovician sediments, however, have been definitely distinguished by fossil evidence, in many places within New South Wales and Victoria. On the other hand certain sedimentary belts within New South Wales have been assigned to this period, not on direct fossil evidence but on general lithological and structural grounds and as being pre-Upper Silurian in age.

David[32] states that the Ordovician rocks of Victoria of a "pelagic graptolite type....extend southwards into Tasmania and northwards into New South Wales right up to the Queensland border.... There a *Diplograptus* has been identified in the local Brisbane Schists, which there belong either to the top of the Ordovician (?) Bunya Series, or to the base of the Silurian (?) Neranleigh Series. A long intermittent belt of Upper Ordovician rocks, characterized by veins of turquoise and other hydrous phosphates, extends from the Ovens River, in Victoria, through Bodalla and Murwillumbah in New South Wales, the Neranleigh and Bunya Series of Brisbane, and the cherts of Gladstone and Yeppoon, to Innisfail, south of Cairns, Queensland. The uniform character of this phosphatic zone suggests a more or less continuous development of Upper Ordovician rocks, along the eastern seaboard of Australia, for the distance of about 1,700 miles."

It is possible that Upper Ordovician sediments may extend along the more coastal portions of eastern Australia, nevertheless there is no definite fossil evidence for such conclusion. The "*Diplograptus*" mentioned by David appears to have been mislaid, and moreover, there is a divergence of opinion as to its organic origin. On the other hand, determinable fossils are abundant in the Upper Ordovician of Victoria and of south-eastern New South Wales.

In Victoria the Upper Ordovician lies eastward of the grand development of the Lower Ordovician. One belt occurs a little west of the meridian of Melbourne, within a structure known as the Riddell Synclinorium; it occurs

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[32] "Explanatory Notes", pp. 39-40.

also as an eastern flank to the Mount William Belt. It occurs also eastward of Melbourne on the western side of the " Walhalla Synclinorium " and associated area, while it appears again on the eastern " side of this and thence over most of eastern Victoria, where not covered by igneous rock, Devonian sediments, and other types ".[33]

Thomas points out that the Upper Ordovician follows conformably on the Lower Ordovician, where observed, and from which it is definitely separated by the graptolite evidence alone. In Upper Ordovician time, the Victorian sea varied in depth " as is shown by the fossiliferous grits (Riddell Grits) which, however, occur at several horizons. Apart from this, the lithology is the same as for the Lower Ordovician rocks." These grits appear to indicate the near neighbourhood of land, and they mark the present known western limit of the Upper Ordovician.

The three divisions of the Upper Ordovician, in ascending succession, within the Romney area, are the Gisbornian, Eastonian, and Bolindian, totalling 2,500 feet of sediments.

In New South Wales, as shown by David,[34] " the Upper Ordovician rocks lie in several parallel belts " of which the most easterly is exposed in the coastal zone. The strike is sinuous, but a little west only of north in general.

A study of the geological map of New South Wales indicates these Upper Ordovician rocks as running sub-parallel with the Silurian for hundreds of miles. No undoubted sediments of Upper Ordovician age are known to occur north of Lat. 32° S. in New South Wales, although some interesting exposures which may belong to this age, if not to an earlier one, occur as far north as Lat. 29° S., passing thence under the sub-horizontal cover of later sediments of the Queensland Platform.

One of the belts of the Upper Ordovician, indicated on the geological map of Australia, passes, with breaks, from Cape Howe, approximately Lat. 38° S., to the Mudgee district, about Lat. 32° S. A second extends from far eastern Victoria to Tomingley, by way of Cooma and Kosciusko, Yass, Grenfell, and Forbes, while a third extends as a wide, highly folded and altered mass from the Mitta Mitta-Kiewa area in eastern Victoria through the Albury-Narrandera district in New South Wales, thence through Yalgogrin, and beyond this, following a curved strike to the

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[33] Thomas, D. E., personal communication.

[34] " Explanatory Notes ", p. 43.

highly crumpled, faulted and altered rocks of Cobar, Girilambone, and the country lying west of the Bogan River as far as Lat. 30° S.

The Victorian members form one almost unbroken mass, except where covered by gently undulating Devonian and other sedimentary types, with traces only of sub-parallel Silurian sediments, whereas, in New South Wales, the sub-parallel belts of the Silurian are very pronounced, the Upper Ordovician belts being concealed in many places along the strike. This suggests that the far eastern Victorian area had emerged much more, at the close of the Ordovician, than had the more northern areas, namely those in New South Wales.

Fig. 3.—Ordovician. Possible Ordovician geosyncline within ancient borderland of Queensland.

In Tasmania the Upper Ordovician has not been distinguished from the Lower Ordovician, and, for the purpose of map preparation, it is assumed that the Ordovician sea covered the eastern portion of the island in great measure.

A few words may be helpful at this stage concerning the probable incoming of a grand and interesting geographic form at the close of the Ordovician. The general distribution of the Lower and Upper Ordovician in Victoria suggests that the vast extent of Lower Ordovician sediments deposited in the area west of the meridian of Melbourne had emerged at the close of that period as a geanticline, thus limiting the Upper Ordovician sedimentation, in great measure, to the eastern portion of the State, the newer and narrower marine way thus formed extending far northwards into eastern and central New South Wales. The marked emergence at this, and at earlier periods, in the western, southern, and central portions of the continent was not accomplished as a strong compressive movement, accompanied by late definite unconformable deposition, but rather as a general undulatory movement accompanied and succeeded by disconformable sedimentation.

Adverting to the discussion of the geographic form mentioned above, it is well known that Howitt described the broad belt of metamorphic rocks in north-eastern Victoria as Lower Silurian (Ordovician) sediments which had been subjected to deep burial and consequent recrystallization with the production thereby of paragneisses and granitoids. "They were later described as unconformably underlying the Ordovician sediments and recorded as of Pre-Cambrian age. Later mapping and petrographic work showed that normal Ordovician sediments pass gradually into schists overfolded at a high angle to the west, and their metamorphosed condition is due to lit-par-lit injection. . . . by granitic magma. This magma occurs in places as large masses, and, in the Tallangatta district, is sheared into orthogneiss. The granitic intrusions are believed to be of Devonian age, while the schists are almost certainly metamorphosed Upper Ordovician sediments."[35]

This belt of altered sediments is very wide, possibly exceeding one hundred miles as a maximum, either in the Mitta Mitta area or that of Albury-Narrandera. In its

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[35] Thomas, D. E., Handbook of Victoria, 1935, pp. 104-105.

continuation northwards into New South Wales, we are indebted to the important work of W. R. Browne,[36] who shows how it passes directly into the paragneisses of Cooma and of the Kosciusko region. Thence it passes into the slates and other altered rocks of Kiandra, the very wide belt of paragneisses extending throughout the Albury and Narrandera districts, and northwards towards the Lachlan River. Its influence may have been felt even as far east as Yass. In the Grenfell-Forbes-Parkes district, which is offset only slightly to the east, possibly by a bend in the general strike, the Upper Silurian sediments consisting of coarse conglomerates, unaltered shales, sandstones, blue limestones, and cherty material, may be noted to possess gentle to moderately high dips. Associated closely with these sediments is a broad auriferous belt consisting of schist, slate, marble, and chert. At Tomingley, which is situated on the northward extension of this auriferous belt, slates occur, in which Upper Ordovician graptolites have been found. Furthermore, the Silurian lies almost sub-horizontally in certain places in the western portion of the area, somewhat resembling the Sydney sandstone (unaltered Triassic) in general appearance and attitude. The Upper Devonian associated with these types lies sub-horizontally in the western portion of the field, and in one place it rests upon a worn down granite, intrusive either into the Upper Ordovician or the Upper Silurian. The natural inference is that the Forbes metamorphic series is pre-Silurian, and, in all probability, is Upper Ordovician.

To the north-north-west lie the Cobar and Girilambone Series, where massive copper and gold deposits of the deep-seated type (" saddles ", " pressure-lenses ", massive pyrrhotite, magnetite, and other replacement bodies) occur in metamorphosed, closely folded and strongly faulted conglomerates, slates, " augen " sandstones, and quartzites. With these are associated strongly folded, but only slightly altered, Upper Silurian conglomerates, quartzites, sandstones, shales, and fossiliferous blue limestones. In the Silurian sediments various small copper and gold deposits occur, but not, so far as has been ascertained to date, of the massive or deep-seated replacement type which characterize the valuable deposits of Cobar and Canbelego.

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[36] " Geology of the Cooma District, New South Wales ", *Jour. Roy. Soc. N.S.W.*, 1914, *48*, 272.

These altered sediments, moreover, appear to be strongly overthrust, especially westwards. They lie in the general line of sinuous strike of the metamorphic series of north-eastern Victoria and of southern New South Wales, and they are considered, tentatively, as the northern continuation of that broad and altered Upper Ordovician belt.

The question naturally arises as to the age of this alteration. As may be inferred from the statements quoted above, there is a belief, among some Victorian geologists at least, that the metamorphism of the Upper Ordovician is due to Devonian intrusions. Recent work in New South Wales indicates that not only Upper Ordovician sediments but also Upper Silurian[37] sediments, in some places in the State, have been definitely metamorphosed and closely folded. Certain Silurian sediments also, in Victoria, are known to be much altered. The peculiar lithological and structural associations of the Cobar, Forbes, Narrandera, Albury, Yass and Mitta Mitta areas, however, suggest that the Upper Ordovician was folded and metamorphosed at the close of the Ordovician and prior to the Silurian, or, at least, the division or divisions of the Silurian with which they are associated.

It is probable that a great geanticline was rising along the wide zone now exposed discontinuously, for 500 or 600 miles in length at least, towards the close of the Ordovician. Its final rising at the close of the Ordovician appears to have divided the ancient seaway into two main sequent portions, an eastern and a western. Whether this was accompanied by the formation of a great geanticline along the Queensland coastal and offshore area is not known, as the first definite age, by fossil contents, assigned to the rocks in that region is in the Upper Silurian. To this epi-Ordovician movement the name Mitta Mitta may, perhaps, be given.

The general discussion, however, of folding activities in Western Australia, Central Australia, South Australia, Tasmania, Victoria, and southern New South Wales, is deferred until after the description of Devonian sedimentation.

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[37] Raggatt, H. G., " Probable Late Silurian Age of Serpentine in.... N.S. Wales ", *Proc. Roy. Soc. N.S.W.*, 1937, *70*, 402-5.

THE SILURIAN.

The passage from Ordovician to Silurian was accompanied by profound topographical changes. The ancient seaway in the Macdonnell Ranges area which had existed, approximately continuously, throughout the Upper Pre-Cambrian, Cambrian, and Ordovician, appears to have disappeared after the close of the Ordovician, the marine conditions passing to Eastern Australia. Flooding of the forelands in post-Ordovician time was less pronounced than in earlier periods, but geosynclinal conditions were still pronounced. Unconformities observed, or inferred from structural data, between the Ordovician and the Silurian indicate, moreover, the proximity of great geanticlines, or sources of Silurian and later sediments.

Silurian sediments, with any approach to full representation, have been noted in one State only, namely Victoria. The sequence in that State, therefore, is selected here for special mention.

Chapman and Thomas[38] subdivide the Silurian, in Victoria, into Keilorian, Melbournian, and Yeringian. "Keilorian is correlated with the Lower Silurian or Llandovery Series in Britain; over these, at Keilor, come beds with *Monograptus riccartonensis*, indicating beds of Middle Silurian or Wenlock age. The Melbournian is correlated with the Lower Ludlow series of the Upper Silurian of Britain, and the Yeringian with the Upper Ludlow." Some authorities, however, would consider that only Lower and Upper Silurian occur in Australia, there being no true Middle (terrestrial) Silurian.

The description of the sediments of unknown age in the Macdonnell area and named the Pertnjara by Madigan, is deferred until the chapter on the Caledonian activities has been reached.

Tasmania.

Rocks of the Silurian system, until recently, were considered to be confined to the western half of the State of Tasmania. More recently, however, the Matthinna Series of north-eastern Tasmania, and considered formerly to be Ordovician in age, have been reported to contain *Hostimella* and other Upper Silurian[39] fossils. The western

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[38] Chapman, F., and Thomas, D. E., "Geology of Victoria", Handbook for Victoria, Aust. and N.Z. Ass. Adv. Sci., Melb., 1935, p. 107.

[39] Cookson, Isabel C., "Occurrence of Fossil Plants at Warrentinna, Tasmania", *Papers and Proc. Roy. Soc. Tasmania,* 1936, pp. 73-77.

exposures occur " in a number of irregular areas in association with the Proterozoic and Cambro-Ordovician rocks of the western districts ".[40] Sediments of this age are folded strongly in places, and their strike is markedly bent and is suggestive of the general plan of the Silurian western geosyncline and the associated geanticline and foreland. Thus in the southern portion of western Tasmania the Silurian sediments occur in two main belts with submeridional trend ; thence they sweep grandly eastwards in the more central portion of the northern coastal area, but apparently resuming a northerly course prior to plunging beneath Bass Strait.

The lowest members of the Silurian are known as the West Coast Conglomerates. These are massive and coarsely textured. Waller found them (1903) conformably underlying the fossiliferous Silurian. " With its intercalated quartzites the series is nearly 2,000 feet thick."[41] Above these conglomerates rest the " Pipestem " Series, consisting of conglomerates, grits, quartzites, and sandstone, while conformable with, and overlying the " Quartzite Series " or southern equivalent of the " Pipe-Stem " Series rests the Gordon River limestone, a massive formation 4,000 feet in thickness and highly fossiliferous. Shales or " slates " occur in thin beds among the limestone beds. Conformably with, and above these, lie the Queen River Series, comprising sandstones, quartzites, shales, " slates ", and limestones. They are crowded with fossil remains, including *Favosites grandipora*, *Halysites*, *Atrypa hemispherica*, *Pentamerus knightii*, *Calymene blumenbachii*, *Pentamerus tasmaniensis*, *Rhynchonella* (*antinasulu*, *borealis*, *capox*, and *cuneata*).

Here also perhaps may be included the Mathinna Series of eastern Tasmania, formerly considered as Ordovician.

Victoria.

The Silurian sediments attain a maximum thickness of 20,000 feet or more in the main sequent geosyncline. The seaways, in Victoria as in Tasmania, became restricted as compared with the Ordovician, especially in Lower Silurian time. Three geanticlines appear to have fed the troughs lying east and west of the Mitta Mitta geanticline. These troughs were sequent geosynclines arising from the

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[40] Nye, P. B., personal communication.

[41] David, T. W. E., " Explanatory Notes ", p. 47.

breaking up of the Ordovician seaway. They may, perhaps, be known as the Goulburn, or Zephyrine, geosyncline lying to the west, and the Coralline geosyncline lying to the east.

The Keilorian, or Lower Silurian, marks a definite departure, lithologically, from the preceding Ordovician, both Lower and Upper. The black mudstones are absent from the Keilorian, and the sandstones are green and more coarsely textured. Widespread, but intra-formational, conglomerates appear, while "occasionally shelly fossils and graptolites may be found, but the well-marked graptolitic bands of Ordovician times are absent".[42]

"No Silurian rocks occur westward of the Mount William-Colbinabbin Ranges"; they are confined, therefore, mainly to the east of the meridian of Melbourne, Eastward of Melbourne they extend in a succession of folds: "the contorted synclinal zone of Melbourne, the Warrandyte anticline with a crumpled zone, the Lilydale syncline, the Mount Easton synclinorium, and the Dark River anticlinorium".[43]

The main seaway was the western or Goulburn (southern extension of Zephyrine) geosyncline, lying between Melbourne and Mt. Wellington, possessing a general trend of a little west of north, although the general trend of the Silurian sediments on the eastern portion of the great geosyncline swings from north-east at the coast to north near Woods Point, thence north-west near Mansfield and west through Rushworth, presenting an enormous curve, over 150 miles in length, with its convexity directed eastwards.

In the Walhalla district the lower members of a large synclinal structure (flanked on both sides by Upper Ordovician sediments) outcrop only. on the eastern side. They consist of 5,000 feet, approximately, of "phyllites, sandstones, and quartzites". The Jordan River beds, higher in the sequence, occur on the western side of the structure, and consist of 5,000 feet, approximately, of shales, sandstones, black shales, with graptolites. Above these lie the Walhalla Series, the youngest of the three divisions of the Silurian in Victoria. The stratigraphic thickness is 10,000 feet, with basal grits and conglomerates.

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[42] Thomas, D. E., personal communication, 1937.

[43] Handbook of Victoria, 1935, p. 106.

Intra-formational grits and conglomerates also occur. "Associated with the upper grits, and forming the highest beds in the series, are the Centennial Beds, with plant remains containing *Zosterophyllum australianum*, *Sporogonites chapmani*, and *Hostimella*.[44]

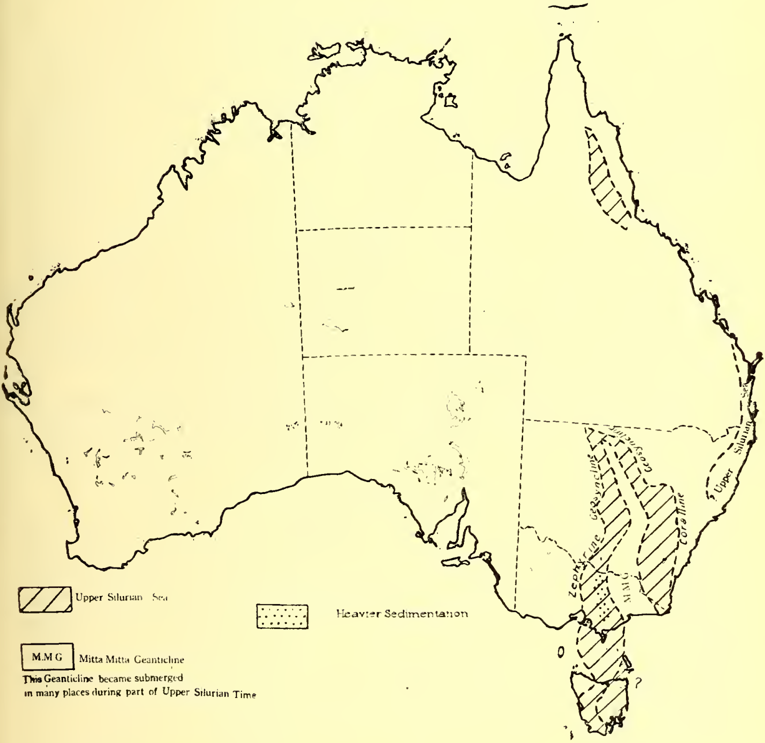

Fig. 4.—The Silurian Sea in New England and Southern Queensland is merely conjectured.

Thomas[45] points out that "In Melbournian times we may get, for the first time, an indication from the sediments which is of use in reconstructing the palæogeography of the period.

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[44] Handbook of Victoria, 1935, p. 108.

[45] Personal communication, 1937.

" There are two kinds of deposit :

" (*a*) *The Western.* Thick fossiliferous sandstones—shelly fossils and graptolites with continuous conditions of sedimentation to the Yeringian. This area lies north and west of Melbourne. . . .

" (*b*) *The Eastern*. . . .Sandstones with thick black mudstones—graptolites and plant remains."

The evidence of the Silurian in eastern Victoria is not nearly so satisfactory as in the Goulburn Geosyncline. Thomas states that it " is impossible to state definitely the correlation of much of the beds in eastern Victoria, sometimes ascribed to the Upper Silurian (i.e. Yeringian) and at others to the Devonian.

" The Wombat Creek section shows these beds resting unconformably on Upper Ordovician, and, in turn, the volcanics (Snowy River porphyries, L. Devonian) rest unconformably on these. Similarly, Middle Devonian limestones, which are strongly folded in part, rest on the Snowy River porphyries. Yet Hills has shown similar igneous rocks rest on Upper Devonian fish beds."[46]

The Silurian is not strongly developed in eastern Victoria in the manner that its northern extension is in New South Wales.

New South Wales.

Lower Silurian has been recorded only from one small area in the State, by Naylor,[47] in the south-eastern portion. The known occurrences of the Silurian are very numerous and cover large areas of the State, nevertheless in almost every instance recorded they are of Upper Silurian (Yeringian) age. They have not been recorded, as yet, on fossil evidence, from any portion of north-eastern New South Wales, that is from the Greater New England Province and its associated coastal and inland slopes. In the south-eastern and central portions of the State they occur in sub-parallel belts arranged east and west of the northern extension of the Mitta Mitta Geanticline, although, in many places, they lie upon this geanticline, where worn down, owing to a marked late-Silurian submergence. Several of these belts are recognized, each being practically continuous (save for breaks due to erosion, igneous intrusion

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[46] Personal communication, 1937.

[47] Naylor, G. F. K., " Geology of the Goulburn District ", *Jour. Roy. Soc. N.S. Wales,* 1935, *69,* 79.

and later-Palæozoic sedimentary cover) for several hundreds of miles, the longest (westernmost) following mainly the curved trend of the Murray River Basin margin, in its southern portion, and that of a contiguous lobe of the Queensland Platform on its eastern side. These trends vary, approximately, from a meridional direction in south-eastern New South Wales to north-west and north-north-west as they are traced northwards through the Condobolin, Cobar, and Bogan districts.

No detailed estimates of stratigraphic thickness for the Silurian in the State have been undertaken, but the magnificent exposures in the eastern, or Coralline, geosyncline of sediments consisting mainly of massive coralline limestones, slates, shales, claystones, and sandstones may be many thousands of feet thick in places.

At Yass the work of Shearsby shows that the Upper Silurian includes the thick Hume beds at the top, these being underlain in succession by the mass of the " No. 3 Porphyry ", the " Yass Beds ", the " No. 2 Porphyry ", the " Bango Beds ", and the " No. 1 Porphyry ". These, in turn, rest upon the Jerrawa Shales, formerly thought to be Upper Silurian, but recently proved by Kathleen Sherrard[48] to be Upper Ordovician, at least in part.

The sediments of the western, or Zephyrine, geosyncline contain massive conglomerates, quartzites, sandstones and other littoral deposits, although fossiliferous limestones, slates, claystones, cherts and other types are present also in places. The sediments of the western geosyncline are probably thicker and more closely folded than those of the complex eastern trough. Shorelines and high feeding grounds appear to have existed in the Yass, Forbes, Cobar, and other western or central districts. The sedimentation in the eastern trough suggests deposition under varying conditions, clear water of shallow to moderate depth in places, coarser deposition along its western margin. Coralline growths are abundant in this eastern trough. Coarse sedimentation appears to have followed the Mitta Mitta Geanticline in New South Wales, especially along its western side. The Yass succession, mentioned above, appears to have taken place alongside the geanticline, or alongside an arc arranged *en echelon* with the main geanticline.

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[48] *Proc. Linn. Soc. N.S. Wales*, 1936, *61*, 4.

In New England a long wide arcuate belt of slate, associated in places, on its western aspect, as in the Armidale district, with a heavy and strongly folded conglomerate, may be traced from the south of the plateau as far north as Lat. 30° S. These sediments appear to be more highly altered than the Devonian sediments adjoining them on the west. The failure to find fossils in this vast exposure to date, together with the general amount of alteration shown by the sediments, suggests an age for them prior to Devonian.

The gently undulating rocks lying to the east of the Willyama Shield may be Silurian or even pre-Silurian littoral deposits. E. J. Kenny[49] considers that some of these types such as the Mootwingee, are counterparts of sediments lying west of Cobar. Silurian and Devonian fossils have been found in the latter.

Queensland.

Silurian sediments, with determinate fossils, have been found only in the Chillagoe district. The geosyncline in which these rocks were deposited has been traced for a great distance. Massive limestones, with sandstones, shales and other sediments of Upper Silurian age have been found therein. The geanticline forming the eastern landmass and the foreland to the west consist of closely folded and altered rocks such as " mica-schists " and " slates ". The continuation southward of the geosyncline is not known; apparently it passed eastward of the present coast, where its sediments have disappeared below the water along with its main feeding geanticline.

Some observers consider that a Silurian sea existed in south-eastern and central Queensland and north-eastern New South Wales.

" . . . such of the argillites of New England as seem to be stratigraphically newer than Upper Ordovician, but older than Lower Devonian, and the rocks of the Neranleigh Series of the Brisbane schists, Queensland, may represent a pelagic type of Silurian sedimentation. In Upper Silurian time the sea transgressed over a considerable area of what is now eastern Australia. Its western boundary extended from a little west of Melbourne northwards to a point west of Cobar, and thence by way of Charleville to at

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[49] Personal communication.

least as far as Chillagoe, in Queensland, and probably, into Dutch New Guinea."[50]

There is no fossil evidence, however, of such supposed existence of Silurian rocks in New England, southern and central Queensland

THE DEVONIAN.

One of the important facts to be noted in the long history of the stabilization of Australia during the Palæozoic is the pronounced volcanic activity which was characteristic of Devonian time.[51]

The Lower Devonian may have representatives in Australia, both marine and terrestrial, but its existence is inferred rather than proved beyond doubt. Such rocks as have been referred to that time appear to consist, mainly, of volcanic and sedimentary types, but unassociated, so far as at present known, with determinate fossils. The Middle Devonian, on the other hand, is mainly a record of heavy marine deposition in well-defined geosynclines, while the Upper Devonian is a record, principally, of sedimentation in the geosynclines carried over, and extended from, the Middle Devonian, with extensive marine flooding of forelands, and of terrestrial deposition associated with later shrinkage of marine areas.

Western Australia.

No sediments of Lower or Middle Devonian age are known from Western Australia. In the Fitzroy River (and associated area) of the Kimberley district, a long tongue of the sea apparently followed an ancient structural depression in Upper Devonian time. The sediments of this age are mainly massive limestones which lie with pronounced unconformity, on early Pre-Cambrian gneisses, and are associated, without apparent marked unconformity, with later Palæozoic sediments.

No Devonian sediments have been recorded from Northern Australia, Central Australia, South Australia, or Tasmania, nevertheless they have a great development in the eastern States of the mainland, namely, Victoria, New South Wales, and Queensland.

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[50] David, T. W. E., "Explanatory Notes", 1932, p. 46.

[51] David, T. W. E., "Explanatory Notes", 1932, p. 48.

Victoria.

Rocks referred by Victorian geologists to the Lower Devonian are represented by lavas and tuffs in a structural depression in the eastern part of the State. These were named the Snowy River Porphyries by Howitt. He estimated their thickness to be 2,000 feet. The Centennial Beds of the Walhalla Geosyncline represent either the uppermost beds of the Silurian, or the lowest beds of the Devonian. These, apparently, are conformable with the Walhalla Series (Upper Silurian), and contain plant remains such as *Zosterophyllum australianum*, *Hostimella*, and *Sporogonites Chapmani*. In this report they are considered as Upper Silurian rather than Devonian.

Middle Devonian rocks are confined to the far-eastern portion of the State, and are recorded as resting unconformably on the Snowy River Porphyries. Breccias and conglomerates pass upwards into tuffaceous shales and interbedded lavas ; and these, in turn, are overlain by massive limestones with fossils such as *Receptaculites australis*, *Phragmoceras subtrigonum*, *Gyroceras*, *Diphyphyllum*, *Spirifer yassensis*, and *Grammysia*. These sediments have suffered rather severely from compression.

Upper Devonian sediments occur over very extensive areas in the State, but are limited in thickness. They have not been subjected at all to severe compression. The sediments also are devoid of marine invertebrate remains. Land plants are common in an excellent state of preservation ; fresh-water fish remains also are common. The rock types include an abundance of lavas, tuffs, conglomerates....“ red and buff tuffcaeous sandstones and blue-grey shales....In the great complex (the Marysville Complex) extending from Warburton to Healesville.... there is a thickness of, at least, 5,000 feet of lavas, and at Mount Wellington, of 2,000 feet....the area originally covered in Victoria (with Upper Devonian) must have been of the order of 10,000 square miles.”[52]

New South Wales.

Lower Devonian is not known, definitely, to occur in the south-eastern portion of the State, but the Middle Devonian is abundantly represented by quartzites, shales, and massive limestones, containing *Receptaculites australis*, *Spirifer yassensis* and *Tryplasma princeps*. Sediments of

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[52] Hills, E. S., Handbook of Victoria, 1935, p. 114.

this age occur at Yarrangobilly, the Murrumbidgee area, Tarago, Cudal,[53] Molong,[53] and Mudgee districts, and elsewhere.

This Middle Devonian sea underwent a profound change in Upper Devonian time. In the earlier portion of this later stage, the Mitta Mitta Geanticline, together with its northern extension, appears to have separated an eastern trough (the Coralline Geosyncline) from a western trough (the Zephyrine Geosyncline). The sedimentation was moderately heavy in several places, and has been estimated variously from 5,000 to 7,000 feet as a maximum. Contemporaneously with this geosynclinal deposition, there appears to have been flooding of the foreland areas to the immediate west.

Marine deposition gave place, in great measure, to continental sedimentation. The Lambian Series, which is the name given to the Upper Devonian of the area under consideration, consists of quartzites containing *Spirifer disjunctus* (and *jaqueti*), *Rhynchonella pleurodon* (and *duni*), *Pteronites pittmani*, and *Lingula gregaria* and *Craspidarges willcaniæ*. Grey, green, and red shales are associated with the beds containing *Lepidodendron australe*, and other forms.

This portion (south-eastern and central western) of New South Wales belongs to the area affected by Caledonian compression, but the north-eastern portion of the State belongs to the area affected by Hercynian compression, and its history presents marked contrasts with that of the more southern and western area.

While the south-eastern massif was completing its stabilization by compression and emergence, the north-eastern area was undergoing active sedimentation in a mobile geosyncline. In this north-eastern area, a great geanticline, or earth undulation, existed, to which the name of " Ancestral New England " may be given. This feature was associated with a parallel western trough, the double topographic form presenting a marked arcuate aspect with its convexity directed westwards and southwards. At the western margin of Ancestral New England, and within a relatively narrow and sinking trough—the New England Geosyncline—the Devonian sediments were deposited in sub-parallel belts. The Lower, or Woolomin Series, of Benson consists of tuffaceous red jaspers and

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[53] Joplin, Germaine A., personal communication.

altered argillaceous sediments, with abundant radiolaria. No determinate fossils have been found in the Series, but its general arrangement and lithology has resulted in its inclusion in the Lower Devonian on the Geological Map of Australia. This pre-Middle Devonian sedimentation is in marked contrast with the activities proceeding, apparently, contemporaneously within the south-eastern massif.

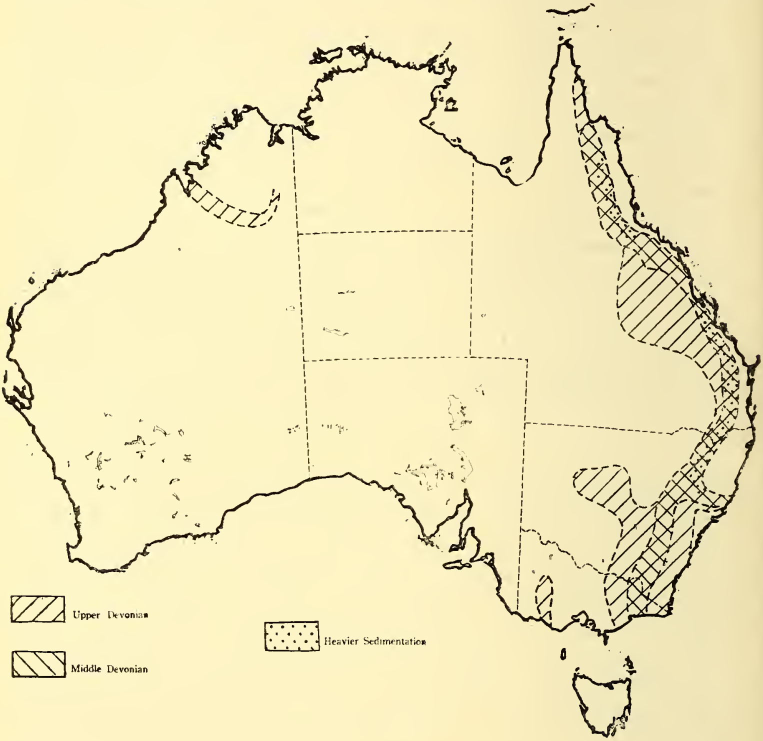

Fig. 5.—The Devonian Period.

The Middle Devonian, or Tamworth Series, of David consists of radiolarian cherts, tuffs, spilitic suites with serpentine, massive limestones with *Sanidophyllum*, *Diphyphyllum*, *Heliolites porosa*, followed by beds containing *Lepidodendron australe*.

The Upper Devonian, or Barraba Series, of Benson commenced with several thousand feet of coarse material, known as the Baldwin Agglomerates, associated with radiolarian claystones. A great thickness of tuffs, mudstones, and shales, with radiolaria, succeeded to these. *Lepidodendron australe* is associated with some of these beds, as it is with certain of the Tamworth beds.

The several groups appear to have been deposited, conformably, and successively, to the west, in a well-marked narrow trough, the deposition amounting to many thousands of feet in thickness.

Queensland.

The important work of Bryan and Reid in compiling and co-ordinating in the light of their extensive field work the immense amount of information[54] extant—but scattered widely throughout mining and general scientific literature, on Queensland geology, has led to the perception of the close relations existing between the middle and later Palæozoic history of New England, in New South Wales, and that of eastern Queensland, a great complex area in which the history of sedimentation, and of later compressive activities, in Palæozoic time, is unique in Australia.

During the Lower Devonian, a structural depression with unfossiliferous sediments appears to have heralded the coming of the important Middle Devonian.

" From the Silverwood area, in south-east Queensland, there has been described a great thickness amounting, at least, to 6,000 feet, of spilitic and andesitic lavas and tuffs. These form the lower part of the Silverwood Series and are assigned a Lower Devonian age."[55]

Radiolarian jaspers in sediments regarded as Lower Devonian occur at Bald Mountain in the same district. In the zone, several hundreds of miles in length, extending from the Queensland-New South Wales border, through Brisbane, Gladstone, and Rockhampton, radiolarian jaspers, " phyllites ", manganese-bearing, and other " schists " have been regarded by some observers as belonging to the Lower Devonian. The non-fossiliferous tuffaceous argillites and " slates ", with grits and conglomerates, and forming the basement of the Middle Devonian north of Rockhampton to Townsville and the Cairns hinterland, have

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[54] Bryan, W. H., " Precambrian and Lower Palæozoic Earth Movements ", *Proc. Roy. Soc. Q'land*, 1925, *37*, 5-75 and references. Reid J. H., " The Queensland Upper Palæozoic Succession " and references, *Publn. No. 278, Q'ld. Geol. Survey*, 1930.

[55] David, T. W. E., " Explanatory Notes ", 1932, p. 53.

been referred also to the Lower Devonian. In one, if not more, places, these basement sediments have an estimated thickness from 9,000 to 10,000 feet.

The evidence for the existence of extensive Middle Devonian sedimentation is eminently satisfactory from the palæontological point of view. The Tamworth Series of the New England Geosyncline, with its coralline limestones, its radiolarian cherts, its spilitic suites and tuffs, and other peculiar forms, has its counterparts in the various mobile geosynclinal zones following the marginal tract of eastern Queensland. The Silverwood area, in south-eastern Queensland, has massive limestones, interbedded tuffs, radiolarian cherts and shales, spilitic suites and massive limestones.

In the Rockhampton area a thickness, estimated at 15,000 feet, of rhyolitic material and interbedded marine limestones, has been observed ; farther north the Ukalunda Series contains limestones, with marine fossils of Middle Devonian types ; in the Burdekin Series, situated far to the north of Ukalunda and Mount Wyatt, a massive limestone, estimated to be about 7,000 feet in thickness, contains forms such as *Gyroceras philpi* and *Phragmoceras subtrigonum* ; while the sediments of the Hodgkinson Series, still farther north, appear to be closely related to the Burdekin Series.

The Upper Devonian is well represented, also, in eastern Queensland, and sediments of this age have been discussed in some detail by Reid in the report mentioned above. He furnishes reasons, based on field observations by himself, Morton, and others, for considering the Star Series of Queensland as belonging to more than one period, a lower series of Upper Devonian (and, in some cases, including Middle Devonian) age, and an upper series, of Lower Carboniferous age. He correlates the Drummond Series also with the Star, the Lower Drummond being the equivalent of the Lower Star, and the Upper Drummond that of the Upper Star. There appear to be two main types of sediment, one predominantly marine, which occurs nearer to the coast in the southern portion of the State, the other resulting from an alternation of marine and terrestrial conditions with a more pronounced tendency to terrestrial conditions. The two related types may have been separated, in some measure, by a geanticline of ancient rocks. In the Silverwood area, definite Upper Devonian sediments do not appear to have been found ; in the

Berserker Range, in the Rockhampton district, a great thickness, about 7,000 feet, of marine tuffaceous, and other material, with Upper Devonian fossils, is recorded. At Rockhampton (coastal basin) also, and in the Drummond Range (inland basin) sediments occur containing *Lepidodendron australe.* At Mount Wyatt, and at Ukalunda, some distance to the north of Rockhampton, and lying within the northern portion of the Drummond area, coloured sandstones abound containing *Lepidodendron australe.* These beds also contain *Spirifer disjunctus.* These again overlie beds with large forms of *Receptaculites australis.*

In the Burdekin Basin one finds coarse conglomerates, probably 2,000 feet in thickness, overlain by red, brown, and other coloured shales, with limestone sparingly developed, the whole being about 5,000 feet thick. The Hodgkinson Series of North Queensland appears to be Upper Devonian in part.[56]

The Devonian sediments in eastern Australia are seen thus to be very thick. Benson estimated the Devonian of New England, exclusive of the Woolomin Series, to be about 26,000 feet in thickness; the maximum thickness of the Devonian sediments in the long Brisbane-Rockhampton trough is estimated at 25,000 feet approximately; and the Burdekin Series is recorded as about 23,000 feet.

THE CALEDONIAN MOVEMENTS (INCLUSIVE OF DEVONIAN).

The close of the Devonian appears to be a fitting stage at which a pause may be made in order to review briefly the main events in the Caledonian orogeny as contrasted with the contemporary happenings in the areas subjected later to Hercynian (and Appalachian) orogeny.

Western Australia.

In the Kimberley District, Wade[57] noted that the Elvire Series (Upper Pre-Cambrian) overlies the early Pre-Cambrian with marked unconformity. Wade noted also an apparent unconformity between the Elvire Series and the overlying Lower Cambrian. Mahony,[58] however,

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[56] Reid, J. H., *ibid.*

[57] Wade, A., "Petroleum Prospects", 1924, Commonwealth Govt., Canberra.

[58] Mahony, D. J., personal communication, 1937.

reports the apparent conformability of the Cambrian and the Elvire, in that portion of the Kimberley area examined by him.

Central Australia.

In the Macdonnell area, Madigan has shown[59] that the Pertaknurra with the Pertatataka (late Pre-Cambrian) overlies the Arunta with marked unconformity. Above the Pertatataka, the Pertaoorrta (Cambrian) and the Larapintine (Ordovician) follow in conformable succession. Conformable with the Larapintine, again, Madigan records the Pertnjara (age discussed later) sediments, 9,000 to 10,000 feet in thickness, and consisting of a dense conglomerate, but in which no fossils have been found. Permian sediments, practically horizontal and unaltered, occur in the eastern portion of the area.

The northern portion of this great group of sediments, with an east-and-west trend, and totalling about 25,000 feet in thickness, has been strongly folded (and apparently overthrust), while to the south the folding appears to pass away in gentle undulations as the massive foreland of Yilgarnia is reached.

South Australia.

In the Flinders Range, and Adelaidean, areas the Adelaidean (late Pre-Cambrian) sediments overlie the early Pre-Cambrian with marked unconformity, while the Lower Cambrian sediments succeed the Adelaidean conformably. The total thickness of Adelaidean and Cambrian is estimated at from 15,000 to 20,000 feet. The great wedge, or prism, of sediments has been closely folded, and appears to have been overthrust to the west or towards Yilgarnia. The Adelaidean sediments thin appreciably to the west and appear to be represented on the foreland of Yilgarnia by relatively thin arenaceous sediments lying sub-horizontally.

Tasmania.

In the island State the "Cambro-Ordovician" overlies the "Pre-Cambrian" with marked unconformity, while the Lower Silurian is recorded as overlying these, in turn, unconformably. Devonian and Carboniferous sediments are absent, while Permian marine and terrestrial sediments

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[59] *Rept. Aust. N.Z. Ass. Adv. Sci.*, 1932, *21*, 76.

lie sub-horizontally, or with gentle undulations, upon the closely-folded Lower Palæozoic formations. In brief, no folding movements, as such term is generally understood, have affected sediments in Tasmania since the Silurian, at the close of which a strong compressive activity occurred.

Victoria.

In this, the south-eastern State of the mainland, the Cambrian, Lower Ordovician and Upper Ordovician are reported to be conformable. All are folded closely, and have the appearance of being more closely folded and altered, in general, than the Silurian. Baragwanath, however, notes the great compression and alteration suffered by the Silurian in certain areas in the Walhalla district. The Silurian also is reported to be conformable with the Ordovician in the Goulburn portion of the Zephyrine Geosyncline. On the eastern side of the Mitta Mitta Geosyncline, however, in the Wombat Creek area, the Silurian has been reported to be unconformable with the Upper Ordovician,[60] but this evidence is called in question by some geologists. The Silurian is not abundantly represented to the east of the Mitta Mitta Geanticline, but the Snowy River Porphyries, referred generally to the Lower Devonian, appear to lie unconformably on the Upper Silurian in the Wombat Creek area.

The Middle Devonian is strongly folded, but without marked metamorphism, while the Upper Devonian lies, usually, in gentle undulations, and with marked unconformity, upon the Middle Devonian.

New South Wales.

In the western portion of this State, the Torrowangee of Mawson, or the Poolamacca (Late Pre-Cambrian) rest with marked unconformity on the Willyama (early Pre-Cambrian) gneisses, while on them, in turn, rest unconformably various unfossiliferous conglomerates, quartzites, sandstones, and shales, which appear to represent early-Palæozoic (pre-Devonian sediments).

On the northern extension of the Mitta Mitta Geanticline, in the Forbes-Parkes area, Upper Silurian conglomerates, sandstones, shales, limestones and argillites occur almost unaltered, although, as indicated above, they are associated with closely folded and altered rocks ascribed to the Upper

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[60] Handbook of Victoria, 1935, p. 106.

Ordovician. Westward of this ancient geanticline the Upper Silurian has been closely folded and metamorphosed definitely also in various places. On the eastern side of the geanticline not only have Lower and Upper Silurian been recorded, but the Upper Silurian, at least, appears to be unconformable[61] with the crumpled and altered Upper Ordovician. Generally speaking, the Silurian of the western or Zephyrine Geosyncline has been subjected to more intense folding and metamorphism than that of the eastern or Coralline Geosyncline.

The close of the Silurian also appears to have been marked by great plutonic intrusions. This remark appears to apply also to Victoria and Tasmania.

The structural relations of the Middle Devonian with the Silurian are not definitely known in this portion of the State. The Upper Devonian is definitely unconformable with the Upper Silurian in some places as Naylor shows, but Germaine Joplin and Alma Culey report conformability in the Cudal-Molong area.

The Woolomin (Lower ? Devonian), Tamworth (Middle Devonian) and Barraba (Upper Devonian) Series, all in New England, are conformable with each other, but the age of the strongly folded complex bounding them on the east is still unknown. The Devonian of New England is conformable also with the Lower Carboniferous. The foreland to the Devonian and Carboniferous activities was the Queensland Platform lying to the immediate west ; the source of the sediments was Ancestral New England lying to the immediate east.

Queensland.

The coastal and highland zone of Queensland with the geanticline (borderland) of Tasmantis to the east is a natural continuation of Greater New England (New South Wales). The only sediments known to be definitely Cambrian and Ordovician in the State are the sub-horizontal and unaltered beds in the extreme west, resting on the old shield of Stuartiana.

Of younger sediments it has been mentioned above that Upper Silurian, with Devonian and Lower Carboniferous, were deposited conformably in the Tasman geosyncline.

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[61] Woolnough, W. G., confirmed by G. D. Osborne, quoted from Naylor, G. F. K., " Geology of the Goulburn District ", *Jour. Roy. Soc. N.S. Wales*, 1935, *69*, 79-81.

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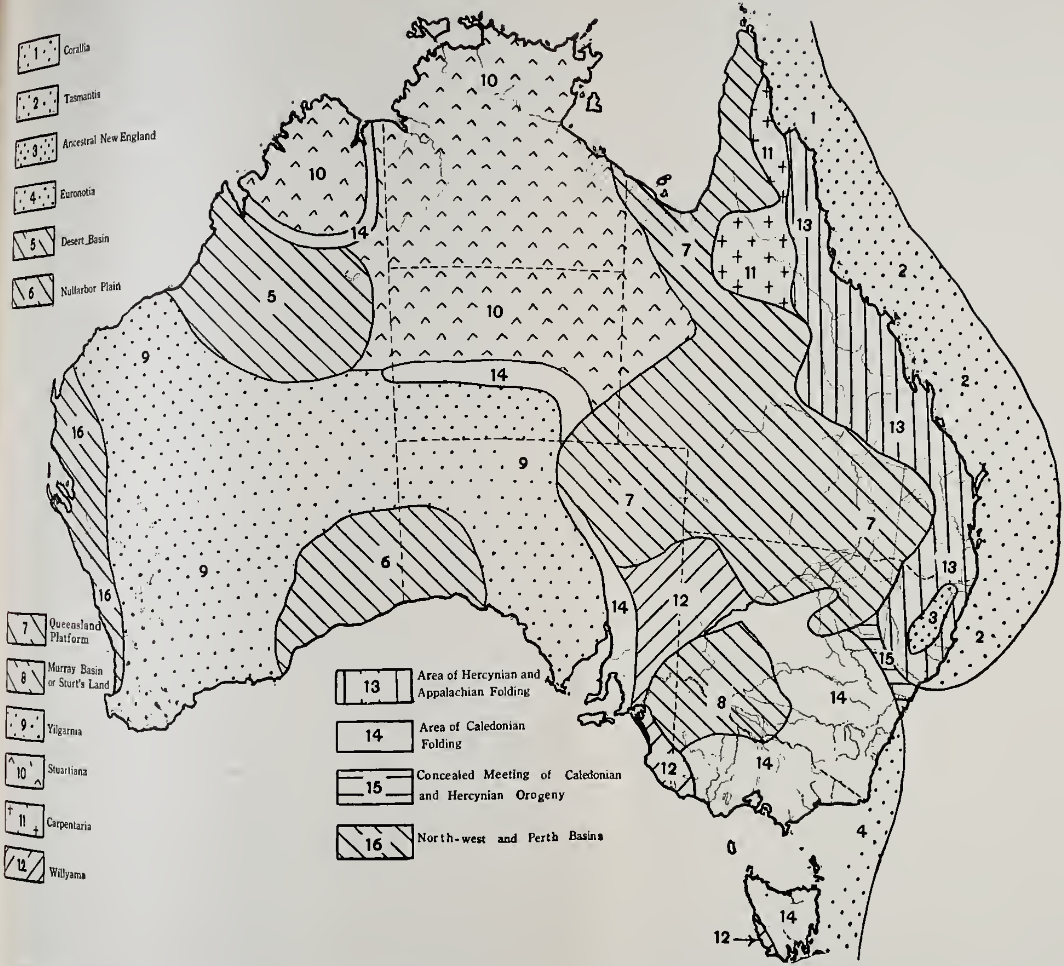

Positive and negative blocks, areas of Caledonian and Hercynian orogeny, and borderlands. The boundaries of the borderlands are not known.

DEDUCTIONS FROM FOREGOING STATEMENT.

The mechanical significance of the foregoing statements indicates the existence in Australia of two great mobile areas possessing contrasted histories, the western and southern one including the Kimberley, Macdonnell, Flinders, Adelaide, Tasmanian, Bendigonian, Zephyrine and Coralline Geosynclines, and the eastern one including the various divisions of the long Tasman Geosyncline. Of these, the former was affected profoundly by Caledonian compression, the latter by Hercynian and Appalachian compression.

The rock structures in the Kimberley area indicate a strong compression which affected the Upper Pre-Cambrian so profoundly as to result in the emergence and relative stability of this great area. At a later stage this area, in part, appears to have been downwarped to receive Upper Devonian and later Palæozoic sediments, but these do not appear to have suffered any severe compression.

Again, far to the east, in the Flindersian and Adelaidean areas, an early Caledonian movement was experienced, whereby the Adelaidean and Lower (with the lower portion of the Middle) Cambrian were folded closely, the great prism of sediments being overturned towards Yilgarnia, while at the same time, the geosynclinal conditions retreated eastward and southward to receive the Middle Cambrian of Victoria. This movement also affected the sediments surrounding the Willyama Block, causing the Torrowangee Series to be closely-folded, where they dipped off the old massif, but inducing only gentle folds within the Torrowangee sediments where they actually lay upon the massif itself.

Sedimentation continued uninterruptedly, apparently, in the Macdonnell Geosyncline, until the close of the Ordovician and also, so far as may be judged from Madigan's sections, until the close of the Pertnjara sedimentation. The whole mass then, about 25,000 feet in thickness, was folded, the northern portion apparently being closely folded and heavily overthrust southward, the intensity of folding dying away in the direction of Yilgarnia.

Thus, apparently, quite early in the history of the Caledonian movement, the great masses of Stuartiana, Yilgarnia, and Willyama had been welded together to form the large western division of Australia extending from Kimberley in the north-west to western Victoria, western New South Wales, and the eastern margin of the Queensland Platform and Carpentaria in the eastern portion of the continent.

The block which was attached next, in order of time, to the continent was Tasmania, where "Cambro-Ordovician" (Ordovician ?) and Silurian sediments have been compressed in a marked manner, partly as the result of an Epi-Ordovician movement and partly as the result of Epi-Silurian compression. Plutonic intrusions on a large scale accompanied this emergence and stabilization.

The block of the continent next to be attached comprises Victoria with western and south-eastern New South Wales. These may be considered together.

As a preface to the discussion of the structural history of this large and complicated area during the Caledonian orogeny, it is a pleasure to record the indebtedness of Australian geologists, generally, to Victorian workers. Their work does not appear to have been recognized sufficiently. Victoria is a State relatively small in area (88,000 square miles approximately), and by some students it may be considered to be an area out of which demonstration might be expected, naturally, to arise concerning Ordovician and Silurian sedimentation, but an impartial consideration indicates that the official Geological Survey of that State, although commenced eighty years ago (under Selwyn), was founded in greatness, and, moreover, that the old traditions of accuracy and thoroughness have been maintained since that inception whenever funds have been available for areal surveys and the publication of field results. It was in this State that the Cambrian was definitely distinguished from the Ordovician, and that in areas of close folding. Here it was that the Lower and Upper Ordovician, in closely folded rocks, were zoned by their fossil contents; here, also, it was that the mining geologists worked out, in detail, the complicated structure of the Cambrian, Ordovician and Silurian sediments in the various great gold fields such as those of Bendigo, Ballarat, and Walhalla. Victoria is the one State in which not only has a clear picture of the complex Cambrian and Ordovician been presented, but the one in which a satisfactory picture of the Silurian has been revealed with its three main divisions. It is a State also in which Lower (?), Middle, and Upper Devonian have been described and their structural relations elucidated. Among the pioneer workers were Selwyn, Howitt, and Murray. (Prior to these, however, in New South Wales, the name of W. B.

Clarke must not be forgotten, the " Father of Australian Geology ", whose herculean and unassisted labours did so much for Australian geology in general.)

The general mass of the rocks west of the meridian of Melbourne are Lower Ordovician, laid down in a great trough which may be known as the Bendigonian Geosyncline. These sediments appear to have emerged at the close of that period. The successor to the Bendigonian Geosyncline appears then to have moved to eastern Victoria and southern (with central) New South Wales, in which a great deposition of Upper Ordovician took place. This wide trough may perhaps be called the Euronotian Geosyncline. It is probable that the site of the later (Silurian) Goulburn Geosyncline was occupied by a geanticline which helped to break up the great seaway of the period.

A difficulty arises at this stage as there is no consensus of opinion as to the ages of Victorian foldings.

" Evidence which has been collected in recent years indicates that epi-Ordovician earth movements in Victoria were either absent or generally of small magnitude, and in most areas the Silurian sediments follow the Ordovician rocks conformably, but with a lithological change, but in eastern Victoria....an unconformity has been recorded."[62]

" Evidence from eastern Victoria indicates that the Upper Devonian intrusives were preceded by an earlier series of granites, possibly, in part, Lower Devonian or epi-Silurian in age, but in view of the uncertain field relations of many of the formations in this little-known part of the State, the actual age and extent of pre-Upper Devonian intrusives cannot be indicated with certainty. At Mt. Taylor, however, granites are overlain by Upper Devonian sediments, and the injection gneisses, granites and granodiorites, of the north-eastern metamorphic belt may perhaps be pre-Middle Devonian....

" It is difficult to assess the value of the evidence at present available with regard to Devonian earth movements, but we know definitely that no strong compressional movements went on in Victoria after the Middle Devonian rocks of Tabberabera, Buchan....had been folded. There is a major unconformity between the Middle and Upper Devonian rocks, the latter series, as a rule, exhibiting gentle dips with open folding....it is possible that, in the eastern

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[62] Chapman, F., and Thomas, D. E., Handbook of Victoria, 1935, p. 106.

parts of the State, the emergence of the geosynclinal deposits began earlier, so that the Lower and Middle Devonian series were deposited on the eroded basement of Ordovician and Silurian rocks and pre-Devonian granites."[63]

A study of the literature, combined with a general personal acquaintance with the Victorian sediments, indicates that there is a high probability of unconformable junctions, in eastern Victoria, between the Upper Ordovician and the Silurian in some places at least; between Upper Silurian and Lower Devonian; and a definite unconformity between Middle and Upper Devonian in the east. The Mitta Mitta Series is now known to owe its intense folding, faulting, and alteration to Caledonian compression and "igneous injection". Moreover, the intensity of the compressions and alterations (metamorphism) suffered by the Ordovician here as compared with the relatively slight alteration induced in the Devonian sediments suggests strongly that their age is pre-Devonian at least. Baragwanath, in a personal communication concerning the Mitta Mitta, states: "This is certainly Pre-Devonian, and almost as certainly Pre-Silurian. The beds are, where not too highly altered, found to be, in the eastern areas, Upper Ordovician. The Devonians are not metamorphosed in any area and, with the exception of a few local strips of high inclination, only slightly warped....the same beds can be followed for scores of miles, so slight is the warping." The Silurian also in the area under consideration presents local patches of intense folding and alteration[64] (and intrusion). Combining this knowledge with the records of the Silurian overlying the Upper Ordovician unconformably in the Coralline Geosyncline and the association of non-metamorphosed Silurian with presumably Ordovician types in the Forbes-Parkes and Cobar districts, it would seem that there was a great epi-Ordovician (Taconic) movement, which produced a long wide geanticline (Mitta Mitta) extending, more or less continuously, with sinuous trend, or in offsetting manner, from eastern Victoria to the Darling River, in New South Wales, by way of the Albury, Cooma, Narrandera, Forbes, and Cobar districts.

This great growing and complex geanticline divided the south-eastern, or Euronotian, Geosyncline into the sequent

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[63] Hills, E. S., Handbook of Victoria, 1934, p. 116.

[64] Baragwanath, W., personal communication, 1937 (for Victoria).

troughs of the Coralline in the east and the Zephyrine (Goulburn in the south, and Cobar in the north) in the west.

Another geanticline appears to have existed offshore named Euronotia, extending from eastern Tasmania to the Hunter River area. The Silurian sedimentation may be expected to be unconformable with the Ordovician where it is closely associated with the Mitta Mitta, or any related geanticline, and yet it may well be conformable in certain spots in the fairways of the sequent geosynclines.

The epi-Silurian also appears to have been a strong compressive movement, as is suggested by the notes above and from the fact that at the close of the Silurian the whole of Tasmania, and the great bulk of Victoria, west of meridian 147° E., together with much of western New South Wales, were never subjected to strong compressive movements after the Silurian folding and plutonic intrusive periods.

In the far eastern portion of Victoria, and possibly, though not at all proved as yet, south-eastern New South Wales, the deposits of Middle Devonian were strongly folded at the close of this grand phase, thus stabilizing the eastern portion of Victoria and the far south-eastern portions of New South Wales.

This epi-Middle Devonian movement, perhaps, may be named the Tabberabbera movement, from its strong effects being first noted at Tabberabbera in eastern Victoria.

At the close of the Upper Devonian a compressive movement, described and named the "Kanimbla"[65] by Sussmilch, affected the sediments of Upper Devonian age both in the eastern and western sequent geosynclines, and a marked period of plutonic intrusions came as a fitting conclusion to the intensive volcanic phenomena of the whole Devonian period. The long seaways, which hitherto had probably been connected in some way with the New England Geosyncline round the northern and western end of the borderland of Euronotia, were shut off at the close of the Devonian and the whole of south-eastern Australia thus, at this stage, became stabilized and attached permanently to the continent. During the epi-Devonian movement in New South Wales, the Devonian of Victoria was subjected only to a mild activity productive of gentle undulations.

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[65] Sussmilch, C. A., "Geology of New South Wales", p. 82. Angus & Robertson, 1914.

In other words, successive compressive movements during the Caledonian stage resulted in the progressive growth of stability for Australia as from west, south, and south-west to north and north-east, and, in this way, areas of former mobility under compression became forelands in succession, against which later Caledonian activities died away in gentle undulations.

There remains for discussion the case of the folded Pertnjara in the Macdonnell area. Madigan considers this great formation of 9,000 to 10,000 feet of conglomerate as probably Permian or Carboniferous in age, from the occurrence of actual Permian sediments lying eastwards of this area, and by analogy with the great Carboniferous conglomerates of New England. The sediments known, more or less definitely, to be Permian, in the east of the Macdonnell area, however, are of unfolded and unaltered nature. The Pertnjara are unfossiliferous, as are the associates of the Torrowangee or Poolamacca on the Willyama complex, and they are located on areas which have been subjected to powerful Caledonian movements. Madigan's work in the Macdonnell area has been of great value to students of the structural history of Australia, and, as the Pertnjara Series appears to be devoid of fossil remains, its age, perhaps, may only be inferred at the present time, but it would seem that the nature of the structural evidence favours a Silurian (or Ordovician ?) age for the Pertnjara, and that a strong epi-Silurian movement is indicated for the main folding of the Macdonnell sediments, the Pertnjara included as being conformable with the earlier associated formations.

THE CARBONIFEROUS.

Contrary altogether to the complicated movements of the closing Ordovician, Silurian, Middle Devonian and Upper Devonian within the great mass of western and southern Australia, the sedimentation of Silurian, Lower, Middle, and Upper Devonian, and of Lower Carboniferous time appears to have proceeded conformably within the Tasman Geosyncline, a trough[66] extending from the Hunter River area in the south to Cape York Peninsula in the north.

The feeding geanticline appears to have been a long borderland of which remnants are to be found along the

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[66] Sussmilch, C. A., "Carboniferous in Eastern Australia", Pres. Add., Sec. C., Proc. A.N.Z.A.A. Science, Melbourne, 1935, p. 83.

Queensland coastal region, but which now, apparently, have sunk beneath the sea in great measure. The name Tasmantis has been given to this ancient borderland by Sussmilch.[67]. Euronotia is a southern continuation, or rather an offset area whose mobility was not so lasting as that of the northern portions. (Plate I.)

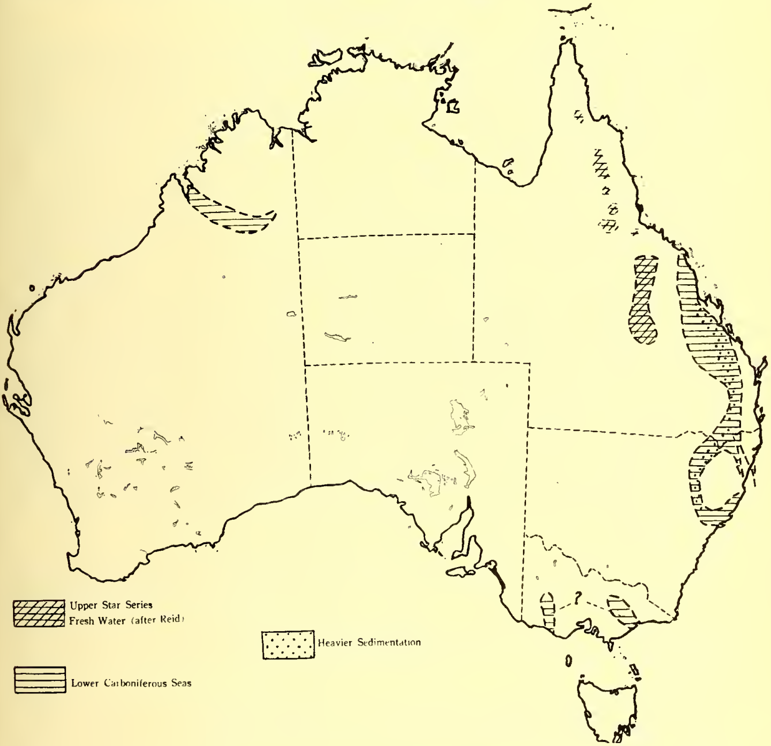

Fig. 6.—Lower Carboniferous.

Western Australia.

Conformably with the Upper Devonian of the Kimberley district, Lower Carboniferous sediments appear to have been deposited in a seaway at least one hundred and fifty miles in length. A coarse conglomerate forms its base, fed apparently from the north.

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[67] Sussmilch, C. A., " Sequence, Glaciation, and Correlation of the Carboniferous Rocks of the Hunter River District, N.S.W.", *Proc. Roy. Soc. N.S.W.*, 1919, *53*, 246.

Victoria.

The Upper Devonian in Victoria appears to pass conformably upwards into terrestrial beds of the Lower Carboniferous. Fish remains are common. The beds are gently undulating in the main.

New South Wales.

With the epi-Devonian (Kanimbla) movement there was a general tendency for emergence throughout the continent, and nowhere does this appear to have been more pronounced than in New South Wales. The whole of the Coralline and Zephyrine sequent geosynclines became dry land, while the main axis of the northern portion of Euronotia, namely that portion within the Nowra-Hunter River area, appears to have passed somewhat eastward. Ancestral New England became prominent again and supplied thick masses of Lower Carboniferous sediments to the New England Geosyncline, the main axis of which had advanced somewhat to the westward (and southward in its southern development). Sussmilch[68] states that at Gloucester this series, which is 10,000 feet thick, consists of oolitic coralline limestones, mudstones and shales containing crinoids, limestones, together with lavas and tuffs. This series is known as the Burindi (of Benson) and is of marine nature. It is grouped with the Tournaisian and Viséan.

Much of our earlier knowledge of this important period is due to the pioneer work of Benson and Sussmilch.[69] Serpentine and related rocks are recorded by Benson as belonging to the Carboniferous in the New England district.

Above the Burindi comes the " Kuttung " of Sussmilch, apparently also within the Lower Carboniferous, by reason of its peculiar *Rhacopteris*, *Cardiopteris*, and *Lepidodendron* contents. For this work in the classification of the Kuttung sediments we are indebted to the palæobotanical determinations of Walkom. Its thickness is estimated at 10,000 feet. It commences with very thick and massive conglomerates derived from Ancestral New England. Volcanic activity, as in the preceding Burindi, Barraba,

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[68] Sussmilch, C. A., " Geology of the Gloucester District ", *Jour. Roy. Soc. N.S.W.*, 1921, *55*, 234.

[69] Benson, W. N., *Proc. Linn. Soc. N.S. Wales*, 1913, *38*, *42*, *43*, 1920, *45*. Sussmilch, C. A., Reports quoted above.

Tamworth, and Woolomin series, is notable, and this is associated, in its less active development, with a grand glacial period. During the greater portion of the Kuttung the sea appears to have retreated from the State. Upper Carboniferous sediments are not definitely known to exist in the State.

Queensland.

Until the recently published works of Bryan, Morton, Reid, Richards, and Whitehouse, ideas as to the Upper Palæozoic succession and structural history of Queensland were not at all clear.

Reid distinguishes between what he calls " central " and " coastal " deposition. The " Star " beds, as mentioned above, appear to him to represent a conformable succession of Upper Devonian (probably also with Middle Devonian) and Lower Carboniferous, the Lower Star being Devonian and the Upper Star being Lower Carboniferous. This Lower Carboniferous or Upper Star, although following the northern coastal area of Queensland in the Carpentaria portion of the Tasman Geosyncline, nevertheless retreats somewhat inland farther to the south, namely in the Capricorn division of Reid. In all cases observed the Upper Star sediments are terrestrial. Reid records these as " probably widespread in Central and Northern Queensland ", all fresh water in nature, and associated with volcanic eruptions. It is the "*Lepidodendron veltheimianum* period ".

These Upper Star beds have marine equivalents lying to the east in the coastal region of the south-eastern portion of the State, being represented there by thick accumulations of " oolitic limestones, which, in many cases, are markedly lenticular, banded cherts which weather beautifully into black and white bands, greenish to dark mudstones and shales, calcareous greywackes, grits, sandstones, and pebble conglomerates. Contemporary volcanics, flows, and tuffs are abundantly developed, of andesitic types, to a dominant degree....The oolitic limestone of Lion Creek is characterized by the occurrence of such genera of first importance as *Lithostrotion* and *Amygdalophyllum*."[70]

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[70] Reid, J. H., " Queensland Upper Palæozoic Succession ", *Publ. Q'land Geol. Surv. No. 278*, 1930, 30.

This marine series, like that of the New England Province in New South Wales, is estimated at many thousands of feet in thickness.

Reid considers[71] that there is a considerable amount of evidence for a " Lower-Carboniferous-Permo-Carboniferous Transition Series ". He bases this belief on the information gained by a correlation of the official field work carried out in Queensland and New South Wales, and on the known distribution of organic forms such as *Monilopora nicholsoni*, *Protoretepora* (*ampla*), *Trachypora wilkinsoni*, *Productus farleyensis*, *Spirifers*, *Martiniopsis*, *Aviculopecten*, *Deltopecten*, *Dielasma*, and so on. On the other hand the field work in New South Wales suggests rather that the upper portion of the Lower Carboniferous there is mainly of terrestrial origin, and that a long period elapsed between Lower Carboniferous and Lower Permian, during which the sea had retreated from the present continental area.

The excellent work of the Queensland geologists indicates definitely, however, that the Greater New England Province is really a southern extension of the Tasman Geosyncline and of the Palæozoic Borderland of Queensland.

THE PERMIAN.

This period in Australian history has been the occasion of marked divergence of opinion among geologists, partly because of the difficulty of fixing its lower limit, and partly because of the faunal differences between sediments of this age in eastern Australia and other areas.

Clarke, Wilkinson, Etheridge, and Jack long ago recognized sediments of this age when conducting surveys on the coal and glacial deposits in the eastern States, while David's later work gave a great impetus to the study of the Permian in northern New South Wales by such workers as W. R. Browne, Carne, Jones, Morrison, Raggatt, and Sussmilch.

The Permian sediments in Australia may be divided into four main groups : the Lower Marine (the Lower Bowen of the Queensland geologists), the Lower Coal Measures, the Upper Marine, and the Upper Coal Measures. Of these the Coal Measures are predominantly, if not wholly, terrestrial in eastern Australia. With the exception of the sediments in the central and southern portions of the

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[71] *Ibid.*, pp. 36-48.

Tasman Geosyncline, the Permian has not been affected materially by compression.

Western Australia.

The western portion of the ancient continental mass appears to have been warped during the Permian, along its more marginal development, thus allowing the accumulation within the depressed portions of considerable thicknesses of sediments both marine and terrestrial in nature. All these sediments dip gently towards the sea, or, as in the example of the Desert Basin, to the more central portion of the basin.

Raggatt[72] states that the total thickness of the Permian in the North-West Basin is, approximately, 7,500 feet; the thickness of the sediments recently examined by Wade[73] within the Desert Basin is approximately 11,000 feet.

South Australia.

The areal extent of known Permian sediments within this stable land block is almost negligible. No marine beds have been described. Remarkably fine examples of glacial activities, however, are recorded thence.

Tasmania.

The Permian (Upper Marine) sea covered a very great portion of central and southern Tasmania, the ancient rock masses in the north-east and west forming boundaries to marine visitations, which were succeeded by conditions of terrestrial deposition. The Permian sediments rest on the stable island block almost unaltered and with sub-horizontal attitude.

Victoria.

Permian deposits are very limited in extent and thickness in this State also. No marine beds have been recorded, but excellent studies of Permian glaciation are to be found therein. The sediments lie almost sub-horizontally, with local exceptions where they have been affected by Tertiary or post-Tertiary warping and faulting.

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[72] Raggatt, H. G., "Geology of North-West Basin", Western Australia, *Jour. Roy. Soc. N.S. Wales*, 1936, *70*, 111.

[73] Wade, A., unpublished.

New South Wales.

The Permian in this State is splendidly developed, and a considerable amount of reliable information is available as to its extent, mode of deposition, and structure, owing to its economic importance as the Main Coal Province. The maximum thickness of the Permian sediments in the Hunter Valley appears to be 14,000 feet,[74] approximately.

The Lower Marine sea covered only a small area in the Hunter Valley area, but another appears to have existed on the eastern side of Ancestral New England, and occupying a sequent geosyncline which came into being possibly during the Carboniferous or even earlier.

The Lower, or Greta, Coal Measures overlapped the southern exposures of the Lower Marine sediments, and terrestrial sediments of this stage appear to be represented near the Queensland border in related troughs.

During the Upper Marine the sea transgressed widely over the Hunter, the Hawkesbury, and neighbouring areas, and this phase, in turn, was succeeded by widely-spread terrestrial conditions productive of coal-seam formations. Glacial conditions, which had been prominent during the upper portion of the Lower Carboniferous (Kuttung), reappeared during both the Lower and Upper Marine Stages. Volcanic action was pronounced almost continuously throughout the Permian, as it had been during the Devonian and Carboniferous in the New England and associated troughs.

The Permian sediments lie almost unaltered, and but slightly disturbed, over the greater portion of the area occupied by them in the State, but, in their eastern development within the New England Geosyncline, they are folded and faulted. In the eastern division of the Tasman Geosyncline—a sequent marine way to which the name Clarence Trough may be given—the Permian sediments have been folded and affected strongly by large and important plutonic intrusions.

Queensland.

The Permian in Queensland is divided into the Lower, Middle, and Upper Bowen. Sediments of this age attain a maximum development in the Great Syncline[75] which extends for many hundreds of miles in south-eastern

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[74] L. J. Jones, Report in preparation.

[75] Reid, J. H., *Publ. Q'land Geol. Surv. No. 278*, 1930, 62, *et seq.*

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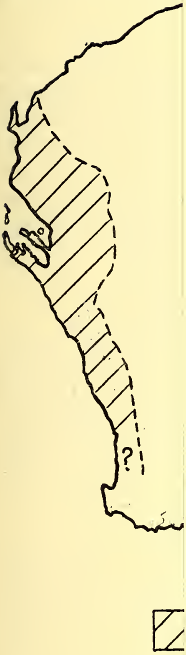

M—September 1,

Fig. 7.—Australia in Permian (Upper Marine) time.

Queensland, but somewhat distant from, although subparallel to, the coast. The occurrence of volcanic and glacial conditions, together with gigantic bituminous coal seams, is to be noted, as in north-eastern and central coastal New South Wales. Very little detailed mapping of the sediments, as a whole, has been carried out, but from the information available Reid estimates a maximum of 8,700 feet thickness for the Lower Bowen in the Stanwell district, of 6,000 feet of marine sediments in the Styx district for the Middle Bowen, and of "over 9,000 feet thickness on the eastern side of the Bowen Syncline". The Upper Bowen is enormously developed at a distance from the coast, but appears to be absent from the coastal area itself, although Middle and Lower Bowen occur in that situation in places.

The more inland exposures of the Permian sediments, as in similar situations in New South Wales, are almost unaltered and possess gentle dips only, whereas the eastern, or coastal, exposures are strongly folded and are intruded by plutonic rocks. This gradual fading away of the influence of compression which is to be noted on a western, or inland, traverse is noticeable also in the Devonian and Carboniferous sediments of eastern Queensland.

Hercynian and Appalachian Movements.

It may now be helpful to attempt a co-ordination of the information gathered from a study of the New England and eastern Queensland areas, with a view to the appreciation of the steps whereby great arcuate belts of Silurian, Devonian, Carboniferous, and Permian rocks in this region were attached successively, as dry land, to the growing continent of Australia.

Benson noted the conformable sequence of the Devonian and Carboniferous rocks of New England. Sussmilch, Browne, Osborne, Carey, and others greatly extended our knowledge of the Carboniferous in the field. These groups, totalling immense thicknesses, probably between 40,000 and 50,000 feet, appeared thus not to have had the same structural history observed in regions farther south, where conformable sequences among the middle and upper Palæozoic sediments were rare. Moreover, Silurian and Ordovician rocks are common in the southern areas, whereas folded Carboniferous is unknown there, Carboniferous sediments being absent altogether from southern New South Wales, while fossil evidence of Silurian or Ordovician sediments in the New England Province is still wanting. Carboniferous sediments, moreover, in New England, are strongly folded.

Other geologists, in Queensland, such as Bryan, Morton, Reid, Richards, and Whitehouse, building on the work of Dunstan, Etheridge, Jack, Jensen (and others), in conjunction with their own extensive field observations, have reached conclusions for eastern Queensland somewhat similar to those of workers in New England.

It has been stated above that the only exact knowledge extant of the age of pre-Devonian activities in the Eastralian Province, north of Euronotia, is that which is associated with Upper Silurian sediments, which were developed in a trough bounded by closely folded and altered sediments, the western groups appearing to be more ancient than those to the east. Devonian, Carboniferous, and Permian sediments appear to have been deposited in an extension of this Silurian trough.

During the epi-Devonian movement ("Kanimbla" of Sussmilch), when the final strips of territory were added to the slowly growing Caledonian mountain area, by which the stability of the continent had been gradually, but surely, winning its widening way, the Devonian sediments in the Tasman Geosyncline still remained unfolded, although the great area affected by the Caledonian orogeny actually appears to have osculated the southern portion of this northern trough. During this final effort of the Caledonian compression, Ancestral New England rose again. This geanticline furnished an immense thickness of Carboniferous sediments into the New England Geosyncline, whose main axis had moved somewhat westward. In Queensland also the sedimentation continued, maintaining a conformable sequence through Silurian (Chillagoe) and Devonian.

The first compression of these sediments in New South Wales appears to have occurred during the Lower Carboniferous. Sussmilch considers that the Burindi and Kuttung are conformable series. The massive Wallarobba Conglomerate forming the base of the Kuttung indicates, however, a great rising of Ancestral New England.

A great deal of difficulty has attended the correlation of Queensland observations by reason of the conflict of early statements. After an analysis of the published information on the subject, Reid states[76]:

"This possibly....appears to favour the following interpretations....The Drummond movement was alone responsible for a mutual folding of the Upper Silurian and Star (Lower Carboniferous, Upper Devonian, and Middle (?) Devonian) beds in North Queensland, that is, possibly no effective orogeny occurred there between Upper Silurian and Late Lower Carboniferous."

This conclusion was reached only after important field notes and collections had been made recently in the Mount Mulligan division of the Hodgkinson (Devonian) beds. This Drummond movement appears to have been powerful, affecting the sediments of the New England Geosyncline, and, according to Reid, affecting the coastal area of Queensland from Cape York to the Townsville district; thence, southward, the movement avoided the wide coastal area and passed inland by way of Ukalunda and the Drummond Range. An overlap of the sub-horizontal Permian beds obscures its southerly continuation thence, but the general field relations suggest that its western limit retreated in a south-easterly direction towards its outcrop again at Texas and Silverspur. The intensity of folding appears to die away definitely as the Queensland Platform is approached, suggesting that the foundation of this huge basin consists of an ancient stable structure which has been unaffected by Middle and Late Palæozoic compression. Benson shows that the remarkable serpentine intrusions and associated volcanic suites of western New England belong to a period of Carboniferous unrest.

It is to be noted that the Carboniferous sediments in northern Queensland containing *Rhacopteris* and *Cardiopteris* do not appear to have been involved in the Drummond movements, but lie unconformably on the Lower Carboniferous containing *Lepidodendron veltheimianum.* Walkom has shown the *Rhacopteris* beds to be Lower Carboniferous, therefore a strong compressive movement is indicated *during* the Lower Carboniferous in this region.

This movement brought about a general emergence of the great area under consideration and the Kuttung (or upper portion of the Lower Carboniferous) sedimentation

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[76] *Publ. Q'land Geol. Surv.. No. 278,* 1930, 92.

ensued. At a later stage the New England Geosyncline moved its axis slightly inland, while in Queensland the main depression moved eastward, sending a tongue into eastern New England. These geosynclines received the heavy deposition of Permian time. Various slight unconformities would appear to have separated certain divisions of the Permian in New South Wales.[77]

Reid[78] states that the late Permian folding in Queensland "affected the present coastal region, up to a maximum width of 160 miles, extending from about Cleveland Bay (Townsville) to the New South Wales border....There was a marked tendency to overthrust westwards, and this seems greatest along the eastern edge of the Great Syncline from Collinsville southward, for, at the former, thrust faulting occurs and severe accompanying compression is shown by the sharp elbow and hairpin bends of the formations with steep tilting....It is noted, in Central Queensland particularly, that the younger beds involved come in progressively westward in a *general* manner (Devonian to Upper Bowen)."

All the Permian in the eastern exposures, even the Upper Bowen, participated in this strong movement, while the Lower Mesozoics rest on their upturned edges with marked unconformity. Farther to the west, however, the lowest Mesozoics are practically conformable with the Permian, the compressive movement of closing Permian time having virtually died out in those areas. This compression, with the accompanying general emergence, was associated in Queensland not only with plutonic intrusions but also with a tendency to form trough depressions westerly of the area affected by the compression.

In New South Wales the simplest explanation of the phenomena, based on present knowledge of the distribution and attitude of the Devonian, Carboniferous, and Permian formations, is that the epi-Devonian movement not only stabilized the mass of Australia outside of Eastralia and the Tasman Geosyncline, but caused a general emergence in the north-east which was associated shortly after with the development of a sequent geosyncline in eastern New England. In this sequent trough were deposited the marine sediments of Carboniferous (?) and Permian time in the Drake, Upper Clarence, Silverwood, and other

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[77] David, T. W. E., "Explanatory Notes", p. 72.

[78] *Publ. Q'land Geol. Surv., No. 278*, 1930, 84-5.

districts. Possibly by way of the Clarence Basin and former offshore area sedimentation in the above areas was connected with the Macleay and Manning deposition.

At the close of the Permian these sediments, in the northern areas, were compressed, and suffered extensive intrusion by plutonics, as at Drake and Rivertree.

This movement may, perhaps, be named the Clarence Movement, because it was first described from Drake, Rivertree, and other localities within the Clarence River drainage. The activity, however, was more strongly marked a little farther north in Queensland.

The compressive activity of the epi-Permian in the Hunter River Valley is instructive. Here, within the eastern portion of the valley, the Upper Permian beds have been compressed and overridden by Carboniferous sediments, whereas a few miles away to the west the folding phenomena die away towards the Caledonian and Pre-Cambrian forelands in gentle undulations. Similarly, folding passes into sub-horizontality from New England to the south and south-west. Recent work by Carey[79] has shown how powerful in the north was this closing Palæozoic movement by which great masses of Kuttung (Lower Carboniferous) have been thrust westward over the Permian. Farther south along the eastern part of the valley, the earlier work of Morrison and Raggatt,[80] and Osborne,[81] first revealed this heavy overthrusting of Carboniferous over Permian.

CONCLUSION.

Australia thus appears to have arrived at its present advanced state of stability by the welding, or knitting together of:

(1) The ancient nuclei: Stuartiana, Yilgarnia, and Willyama during the Caledonian orogeny taken in a broad sense (inclusive of Devonian movements).

(2) The western strip of ancient "Tasmantis" with (*a*) that part of ancient Stuartiana now known as Carpentaria and the Australian Platform, and (*b*) the area affected by Caledonian foldings. This latter knitting

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[79] Carey, S. W., "Geological Structure of the Werrie Basin", *Proc. Linn. Soc. N.S. Wales*, 1934, *59*, 356.

[80] Morrison, M., and Raggatt, H. G., "Singleton-Muswellbrook Coal-Field", *Ann. Rept. Dept. Mines, N.S. Wales*, 1928, pp. 110-111.

[81] Osborne, G. D., "The Carboniferous Rocks....Hunter River District", *Proc. Linn. Soc. N.S. Wales*, 1928, *53*, 565.

action occurred during the Hercynian (inclusive of Appalachian) orogeny.

(3) The sediments affected by Caledonian and Hercynian activities were deposited in long-enduring geosynclines with complex histories. The stability of the continent which had been attained through the marked folding of these geosynclinal sediments by Caledonian and later Palæozoic activities progressed, generally, as from west to east, but, more specifically, as from south-west to north-east in eastern Australia. In Queensland, however, the later Palæozoic foldings moved from west to east.

The greater portion of the old borderland "Tasmantis" has now sunk beneath the sea, as a compensatory movement to the undulatory rise of the Eastern Australian Highlands, during Tertiary and post-Tertiary time.

A NOTE ON SHORTT CLOCK NUMBER 8 AT SYDNEY OBSERVATORY.

By H. W. Wood, M.Sc.

(*Manuscript received, August 17, 1937. Read, September 1, 1937.*)

Since April, 1936, some time has been devoted to Shortt Clock Number 8 at Sydney Observatory. The clock has been in use as the standard sidereal clock since the beginning of May, 1937.

The clock is contained in a small brick room which is situated in the cellar of the building. The internal dimensions of the clock chamber are 4 ft. × 4 ft. × 6¾ ft. high. The copper case of the free pendulum is fastened by four ½-inch bolts to the old stone wall of the cellar, about 3 ft. thick.

The losing rate of these clocks decreases with reduction of pressure until a minimum is reached, when further reduction of pressure increases the rate on account of increase of the arc of the pendulum. It is obviously advantageous to run the clock at this minimum value, as small changes in pressure would have less effect on the rate. This effect is well known(1) (2) and the clock has been run at a variety of pressures in order to determine where its minimum rate occurs. The performance is similar to that of other Shortt clocks. No trouble has been experienced in keeping the case air-tight.

A graduated scale attached to the lower end of the pendulum and read by a microscope is provided for reading the arc of the pendulum. Due to deterioration of the scale the arc was read only with difficulty and no great precision in 1936. While the clock has been sealed further deterioration has occurred (perhaps due to attack by mercury vapour from the pressure gauge(3)) and reading is now almost impossible. It seemed, however, desirable to try some quantitative explanation of change of rate with pressure.

Variation of the clock rate depends on change of period of the pendulum due to

(1) change of arc,
(2) change of pressure,
(3) change of temperature.

The arc, of course, depends on the rate of supply of energy to the pendulum and the pressure.

The period of a pendulum is given by

$$P_\alpha = P_0\left(1+\frac{1}{4}\sin^2\frac{\alpha}{2}+\frac{9}{64}\sin^4\frac{\alpha}{2}+\ldots\right)$$

α being the semi-amplitude of the pendulum. The correction due to arc keeping the square terms is

$$\frac{\alpha^2}{16}\cdot P_0 \;(\alpha \text{ in radians})$$

making an increase in daily rate due to arc

$$\alpha^2\times 4\cdot 569\times 10^{-4} \text{ secs. per day} \ldots\ldots\ldots\ldots (A)$$

α being the semi-amplitude in minutes of arc.

On energy considerations an approximate representation of the relation between pressure and arc might be given by

$$c_2p\alpha^2+c_1\,\alpha-c=o \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (B)$$

where c_2, c_1, and c are constants and p is the pressure. The first term corresponds to the energy loss per second due to a force varying as the pressure and velocity of swing. The second term is the friction-viscosity loss, and the third term the energy supply per second. Using some observed values of arc we obtain

$$\left.\begin{aligned} c &= 69\cdot 4\ c_1 \\ c_1 &= 585\times c_2 \end{aligned}\right\} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (D)$$

$$p=\frac{40600}{\alpha^2}-\frac{585}{\alpha^2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (E)$$

Where p is expressed in centimetres of mercury and α in minutes of arc. After corrections for arc represented in (A) and (E) are applied, there remain corrections for temperature and pressure.

The daily rate increases 0·263 second per day for each centimetre of mercury rise in pressure...............(F)

The temperature coefficient of the clock is +0·0059 second per day per degree centigrade. The values found for Shortt 3 and Shortt 11 were $0^s\cdot 00508$ and $0^s\cdot 00454$ respectively.(3)

When the clock was first sealed the weight to be left on the free pendulum was wrongly estimated and the clock had a gaining rate of almost two seconds per day. Fig. 1 shows the variation of rate with pressure according to these formulæ. The curve has been drawn using the value —3·995s.+corrections found from the relations (A), (E) and (F). The crosses represent observed rates, corrected to 15·3° C.

The minimum occurs near 1·5 centimetres pressure. This is a little lower than the pressure found for Shortt 3⁽¹⁾ at Greenwich. The clock is being used with the pressure in the case 1·64 centimetres of mercury.

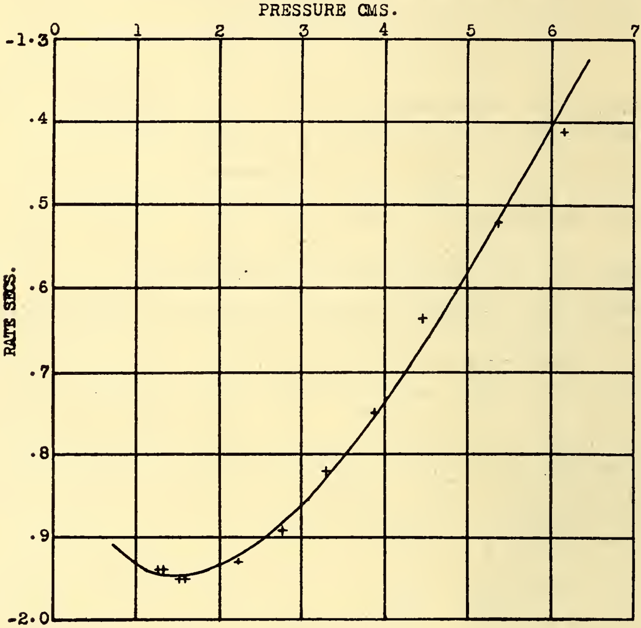

FIG. 1.

The weight on the free pendulum has been altered and the following are some errors of the clock from transit observations since May 28.

There is a secular increase of rate of 0·020 second per day per hundred days, so that the daily rate is given by

$$-0^{s}\cdot0538+0^{s}\cdot020t+0^{s}\cdot0059\ (T^{\circ}-14\cdot9),$$

where t is measured in units of one hundred days and T in degrees centigrade. This is similar to the rates of the Shortt clocks Number 3 and Number 11⁽⁴⁾ at Greenwich.

Date.	Clock Error. (Slow.)	Rate. (Gaining.)	Average T° C.
	s.	s.	
May 28	20·34	—	0
June 10	19·636	0·0538	14·9
July 1	18·341	0·0617	14·1
July 26	16·957	0·0554	13·3
August 5 . .	16·437	0·0520	13·2

Using the relations (D) and taking the pressure as 1·64 cms. of mercury, equation (B) becomes

$$4{\cdot}04\times10^{-5}c\alpha^2+1{\cdot}44\times10^{-2}c\alpha=(c+d),$$

where the rate of energy supply is now regarded as variable by a quantity d. α is the semi-amplitude in minutes of arc. According to this relation a variation of one-third per cent. in the energy supply would change the semi-arc by about 10″. This corresponds to a change in daily rate of almost a hundredth of a second. The rate of supply of energy to the clock is 0·083 centimetre gramme per half minute, about a fortieth of which is lost in friction on the impulse wheel and pivots.(5) A change of about a seventh of the value of the frictional losses would thus cause a change in arc and rate, which is quite large for these clocks. It seems that some of the irregularities which have been observed in this and other clocks(6) must be due to this cause.

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(2) A. L. Loomis: *Monthly Notices Roy. Astron. Soc.*, 1931, *91*.
(3) J. Jackson: *Monthly Notices Roy. Astron. Soc.*, 1929, *89*, 247.
(4) ———: *Monthly Notices Roy. Astron. Soc.*, 1929, *89*, 243.
(5) F. Hope-Jones: Electric Clocks, p. 225.
(6) Jöran M. Ramberg: *Arkiv För Matematik, Astronomi Och Fysik*, Band 25A, No. 20.

SYNTHETIC SUBSTANCES ALLIED TO STRYCHNINE.

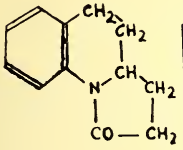
By Francis Lions, B.Sc., Ph.D.

(*Manuscript received, August 18, 1937. Read, September 1, 1937.*)

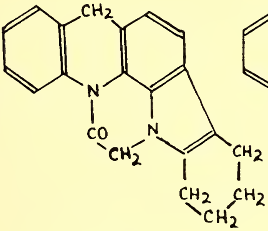
A recent paper by Openshaw and Robinson (*J.C.S.*, 1937, 941) describes certain preliminary experiments on the synthesis of substances allied to strychnine. About twelve years ago Professor Robinson suggested to the author that he should carry out some experiments having a bearing on the question of the constitution of strychnine, and a number of preliminary experiments were made at the time. These were later elaborated and a few of the results recorded by Openshaw and Robinson had already been obtained by the author some years before. Changes in the conception of the constitution of the strychnine molecule removed the need for a completion of the earlier projected experiments and the results remained fragmentary. However, they are now collected and placed on record.

Strychnine and brucine have long been known to contain an acid amide grouping, and it is now fairly definitely established that the nitrogen atom of this grouping is part of a dihydroindole nucleus (cf. e.g. Robinson, Bakerian Lecture, *Proc. Roy. Soc. London*, 1931, *130*A, 431). For a long time this nitrogen was held to be present in a reduced quinoline nucleus. Koenigs (*Berichte*, 1900, *33*, 218) had shown that tetrahydroquinolyl-2-β-propionic acid lactam (I), closely resembles strychnine in many of its reactions, particularly in the ease with which the lactam ring can be opened by the action of sodium ethoxide and closed again with acid, just as strychnine can be converted to strychnic acid and this again cyclised to strychnine.

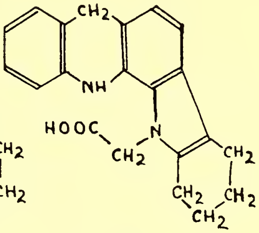
Clemo, Perkin and Robinson (*J.C.S.*, 1924, 1763), also, in a long synthetical investigation of substances having formulæ closely related to that put forward by Perkin and Robinson in 1910 (*J.C.S.*, *97*, 305) for strychnine, showed that anhydrohexahydroacrindoline acetic acid (II) reacted readily with methyl alcoholic potassium hydroxide to give hexahydroacrindoline acetic acid (III), which was again readily cyclised to (II) with boiling hydrochloric acid.



I.

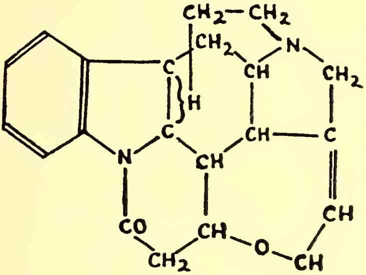


II.



III.

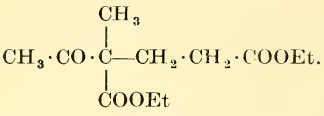
At the present time the accepted formula for strychnine is (IV) (cf. Openshaw and Robinson, *loc. cit.*). It will be observed that the lactam ring of Koenig's compound (I)



IV.

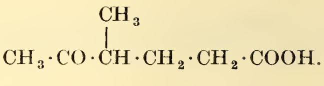
is five-membered, whilst in (II) the lactam ring contains two nitrogen atoms. In strychnine the lactam ring is a piperidone ring. It seemed to be of interest, therefore, to attempt the preparation of some lactams containing a six-membered lactam ring fused with a dihydro indole or tetrahydroquinoline ring system and to examine their general behaviour.

In the first experiments ethyl β-chloropropionate was condensed with the sodium derivative of ethyl α-acetyl propionate and the resulting α-acetyl-α-methyl glutaric ester (V) hydrolysed by heating with dilute acid to γ-acetyl-n-valeric acid (VI). Condensation of this acid with



$$\mathrm{CH_3\cdot CO\cdot \underset{\displaystyle COOEt}{\overset{\displaystyle CH_3}{C}}—CH_2\cdot CH_2\cdot COOEt.}$$

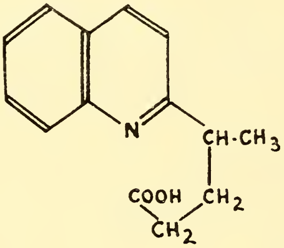
V.



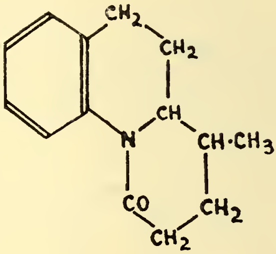
$$\mathrm{CH_3\cdot CO\cdot \overset{\displaystyle CH_3}{CH}\cdot CH_2\cdot CH_2\cdot COOH.}$$

VI.

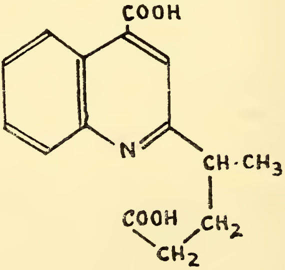
o-aminobenzaldehyde in presence of alcoholic sodium hydroxide solution yielded quinoline-2-γ-valeric acid (VII), which was readily reduced in alkaline solution by sodium amalgam to the sodium salt of 1 : 2 : 3 : 4-tetrahydroquinoline 2-γ-valeric acid. Acidification of this salt leads to rapid cyclisation and the cyclic amide (VIII) can be isolated. It can be readily recrystallised from petroleum ether and comes out in beautiful white needles melting at 80°. Like strychnine it exhibits an Otto reaction, its solution in 60% sulphuric acid giving a transient deep purple coloration on the addition of a trace of aqueous potassium dichromate. Condensation of the acid (VI)



VII.



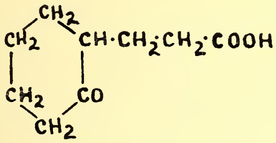
VIII.



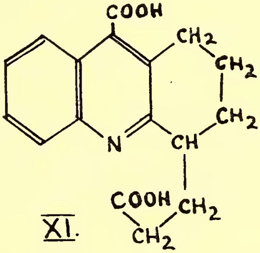
IX.

with isatic acid in strongly alkaline aqueous solution (Pfitzinger's reaction) led to the formation of the quinoline dicarboxylic acid (IX) but attempts to decarboxylate this to (VII) led to no isolable product.

In a second series of experiments ethyl cyclohexanone-2-carboxylate was converted into its potassio derivative in alcoholic solution and this reacted with ethyl β-chloropropionate to give the ethyl 2-carbethoxycyclohexanone-2-β-propionate previously described by Haworth and Mavin (*J.C.S.*, 1933, 1012) and by Openshaw and Robinson (*loc. cit.*). The use of potassium leads to great ease of preparation and yields of 80% or better—at least as high as those previously recorded. Hydrolysis of this ester with boiling strong hydrochloric acid gives cyclohexanone-2-β-propionic acid (X) in excellent yield. When rigidly purified this acid melts at 62°. Haworth and Mavin and Openshaw and Robinson give the melting point as 55°. Condensation of (X) with isatic acid in strongly alkaline aqueous solution yields 5-carboxy-1 : 2 : 3 : 4-tetrahydroacridine-1-β-propionic acid (XI), a very insoluble substance, which melts at 307-8° with decomposition and formation of a very thick dark brown oil. By extraction of this crude reaction product with alkali a small yield only of a yellowish crystalline solid acid could be obtained, later proved to be 1 : 2 : 3 : 4-tetrahydroacridine-1-β-propionic acid (XII). Much of the remainder of the product obtained from the decarboxylation process is readily soluble in ether, the solution exhibiting an intense green fluorescence. Removal of the solvent leaves a heavy, viscous, golden yellow oil. This readily forms an oily picrate and a methiodide and is probably 1-ethyl-1 : 2 : 3 : 4-tetrahydroacridine, contaminated with some 1-ethyl acridine which causes the fluorescence. In further experiments to effect decarboxylation to the acid (XII) advantage was taken of the fact



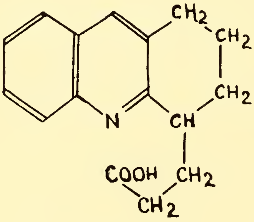
X.



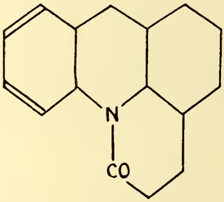
XI.

that cinchoninic acids are not readily esterified. Refluxing an absolute alcoholic solution of the acid (XI) containing a little concentrated sulphuric acid led to formation of ethyl 5-carboxy-1 : 2 : 3 : 4-tetrahydroacridine-1-β-propionate in good yield, and heat treatment of this ester leads to decarboxylation and formation of ethyl 1 : 2 : 3 : 4-tetrahydroacridine-1-β-propionate, from which the acid (XII) is readily obtained by hydrolysis. A more convenient method of preparation of this acid (XII) in good yield was found to be the condensation of the ketonic acid (X) with o-aminobenzaldehyde in presence of alcoholic sodium hydroxide solution.

Reduction of (XII) with sodium and absolute alcohol leads to formation of the sodium salt of octahydroacridine-1-β-propionic acid, from which a cyclic lactam (XIII) can be readily obtained by treatment with mineral acid. It resembles strychnine and the cyclic lactam (VIII) in giving an Otto reaction.



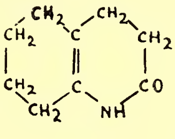
XII.



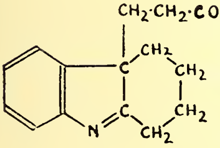
XIII.

The acid (X) is readily esterified and its methyl and ethyl esters are described in the experimental section. Treatment of these with concentrated aqueous ammonia leads rapidly to formation of the crystalline amide, cyclohexanone-2-β-propionamide. This loses water on heating above its melting point and cyclises to the lactam, 2-keto-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroquinoline (XIV).

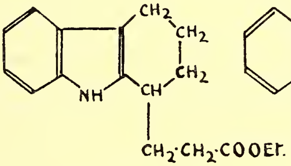
Admixture of the ethyl ester of (X) with phenylhydrazine leads to separation of water and formation of an oily phenylhydrazone, which cyclises readily in boiling glacial acetic acid to ethyl-1 : 2 : 3 : 4-tetrahydrocarbazolenine-11-β-propionate (XV), the yield being almost quantitative. It is remarkable that none of the 1 : 2 : 3 : 4-tetrahydrocarbazole-1-β-propionic ester (XVI), or the corresponding lactam (XVII) is obtained in this cyclisation. Openshaw and Robinson (*loc. cit.*) reported that cyclisation of the phenylhydrazone of (X) with dilute sulphuric acid yields mainly the lactam (XVII) and relatively small amounts of the carbazolenine acid corresponding to (XV). This acid, melting at 226°, can be obtained from the ester (XV)



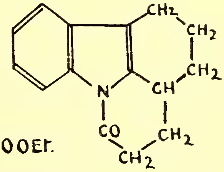
XIV.



XV.



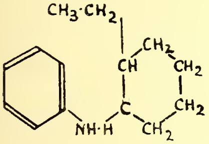
XVI.



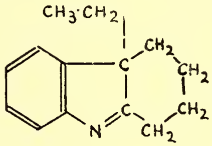
XVII.

by hydrolysis. The methiodide of the ester (XV) is readily prepared and melts at 165°.

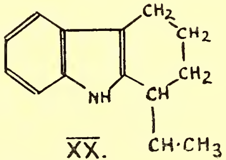
The failure to obtain any tetrahydrocarbazole derivative in the cyclisation of the phenylhydrazone of the ester of (X) led to some experiments on the cyclisation of the



XVIII.



XIX.



XX.

phenyl hydrazone of 2-ethyl cyclohexanone. Plancher and Testoni (*Gazzetta*, 1900, *30*, ii, 558; *R.A.L.*, 1900 (v), *9*, i, 218) have shown that the phenyl hydrazone of 2-methyl cyclohexanone undergoes the Fischer indole synthesis to give a mixture of 11-methyl-1 : 2 : 3 : 4-tetrahydrocarbazolenine and 1-methyl-1 : 2 : 3 : 4-tetrahydrocarbazole; and similar behaviour is shown by the phenyl hydrazone of 2-ethyl cyclohexanone (XVIII), which cyclises readily in boiling glacial acetic acid solution to 11-ethyl-1 : 2 : 3 : 4-tetrahydrocarbazolenine (XIX), which is the main product, and a small amount of 1-ethyl-1 : 2 : 3 : 4-tetrahydrocarbazole (XX). The base (XIX) is remarkable in that it reacts with methyl iodide to form a methiodide which can be obtained in a (labile) yellow form melting at 153° and a (stable) red form melting at 94°. The ethiodide melts at 192°.

EXPERIMENTAL.

Diethyl α-acetyl-α-methyl glutarate (V).

This ester has been previously prepared by Wislicenus and Limpach (*Annalen*, *192*, 133) and by Clemo and Welch (*J.C.S.*, 1928, 2627). The former authors reacted sodio α-acetylpropionic ester with β-iodopropionic ester and obtained a product boiling at 280–281°. Clemo and Welch used β-chloropropionic ester and claimed a 60% yield of product. Experiments in which β-chloropropionic ester has been reacted with sodio α-acetylpropionic ester or with potassio α-acetyl propionic ester confirmed Clemo and Welch's observations. No special advantage follows the use of potassium, and the yield of required ester was 60% approximately by either method, the product boiling at 165–7°/20 mm. or 156–8°/16 mm.

γ-Acetyl-n-valeric acid (VI).

March (*A. Ch.* (7), *26*, 337) prepared this acid as an oil, b.p. 168–9°/22 mm., by saponification of the corresponding ester, which he obtained by the action of methyl iodide and sodium ethoxide on ethyl γγ-diacetyl butyrate. It was prepared by refluxing the ester (V) (50 g.) with a solution of concentrated hydrochloric acid (80 c.c.) in water (240 c.c.) for 3 hours. The cooled acid liquid was saturated with ammonium sulphate and the separated yellow oil taken up and dried in ether. After removal of the solvent the residual oil was fractionated *in vacuo*. The pure acid (24 g.) boiled at 148–151°/11 mm.

Found: C=58·0, H=8·1%; calculated for $C_7H_{12}O_3$, C=58·3, H=8·3%.

Treatment of this acid with a hot aqueous solution of semicarbazide acetate led to formation of an oily semicarbazone, which was induced to crystallise. After recrystallisation from hot water it melted indefinitely between 130° and 140°, but after two recrystallisations from absolute methyl alcohol it was obtained in colourless needles melting at 159–162° with decomposition.

Found: N=21·1%; calculated for $C_8H_{15}O_3N_3$, N=20·9%.

March (*loc. cit.*) gave the melting point as 152–158° after recrystallisation from water.

Quinoline-2-γ-valeric acid (VII).

γ-Acetyl-n-valeric acid (4 g.) and o-aminobenzaldehyde (3·5 g.) were added to a solution of sodium hydroxide (1·5 g.) in alcohol (25 c.c.). After standing 3 days the solution was gently refluxed for 1 hour, cooled, diluted with water and extracted with ether. It was then made just acid with acetic acid and again extracted several times with ether. From these combined extracts, after drying and removal of the solvent, an oil (4 g.) was isolated and induced to crystallise. It was purified by recrystallisation from ethyl acetate and obtained in colourless prisms, m.p. 133°.

Found: C=73·1, H=6·8%; calculated for $C_{14}H_{15}O_2N$, C=73·2, H=6·6%.

This quinoline acid is readily soluble in most of the usual organic solvents, and also dissolves readily in dilute mineral acids or alkalies.

Anhydride of 1 : 2 : 3 : 4-Tetrahydroquinoline-2-γ-valeric acid (VIII).

The quinoline acid (VII) (5 g.) was suspended in water (180 c.c.) and 4% sodium amalgam (180 g.) gradually added. When the acid had completely dissolved carbon dioxide was kept bubbling through the solution. One hour after completion of the addition of the amalgam the mixture was heated to 100° and maintained at this temperature for 12 hours. The cooled aqueous solution was carefully acidified with hydrochloric acid and then heated to boiling for 10 minutes. After cooling it was extracted with ether, and after washing and drying the ether was boiled off. The residual pale yellow oil solidified on cooling. It was very soluble in the usual organic solvents but crystallised beautifully from petroleum ether in fine long colourless needles which melted at 80°. Yield 3 grams.

Found: C=77·9, H=8·0, N=6·5%; calculated for $C_{14}H_{17}ON$, C=78·1, H=7·9, N=6·5%.

A solution of the substance in 60% sulphuric acid gave a transient deep purple colouration on the addition of a trace of aqueous potassium dichromate. The colour faded fairly rapirly but could readily be recovered by addition of more dichromate.

4-Carboxy-quinoline-2-γ-valeric acid (*IX*).

To a solution of isatin (8·3 g.) in aqueous potassium hydroxide solution (45 c.c. of 33%) was added γ-acetyl-n-valeric acid (7·2 g.) and the solution warmed on the water-bath for 6 hours. The diluted solution was then decolourised with charcoal and after filtration acidified with acetic acid. On allowing to stand the quinoline dicarboxylic acid soon deposited as a creamy precipitate, which was collected and recrystallised from ethyl alcohol, being obtained in colourless prisms, m.p. 248–9°.

Found: C=65·7, H=5·7%; calculated for $C_{15}H_{15}O_4N$, C=66·0, H=5·5%.

This acid readily loses CO_2 on heating above its melting point, but it was not found possible to isolate the acid (VII) from the oily product.

Ethyl-2-carbethoxycyclohexanone-2-β-propionate.

As previously mentioned, this ester has been obtained before by reacting ethyl β-chloropropionate with sodio ethyl cyclohexanone-2-carboxylate. This sodio derivative is only sparingly soluble in alcohol. On the other hand the potassium derivative of ethyl cyclohexanone-2-carboxylate is very soluble in alcohol, and reacts readily with alkyl halides. Addition of ethyl cyclohexanone-2-carboxylate to a suspension of powdered potassium in dry toluene leads to a vigorous reaction and the metal goes into solution. Boiling of this solution leads to precipitation of a gelatinous mass which redissolves almost completely on cooling. Addition of an alkyl halide, even in large excess, and prolonged boiling of the resultant solutions, lead to no separation of potassium halide, and it is evident that the potassium is completely co-ordinated. Addition of an ionising solvent such as alcohol to the toluene solution of potassio derivative and alkyl halide enables alkylation to occur. The method finally worked out for the preparation of ethyl-2-carbethoxycyclohexanone-2-β-propionate was as follows: Ethyl cyclohexanone-2-carboxylate (220 g.) was carefully added to a cooled solution of metallic potassium (50 g.) in absolute ethyl alcohol (230 c.c.), the solution thoroughly mixed and allowed to stand 5 minutes. Ethyl β-chloropropionate (210 g.; excess, 1·2 mols.) was then added in small portions with vigorous shaking and efficient cooling. A lively reaction set in immediately and potassium chloride was precipitated. After standing overnight the mixture was refluxed from an oil bath at 140° for 3 hours. Ice-water (1,000 c.c.) was added to the cooled alcoholic solution and the precipitated heavy yellow oil taken up in ether, washed free from alcohol, dried, and the solvent removed. The residual oil was fractionated *in vacuo* and the fraction boiling at 156–8°/2 mm. (256 g.; 80% of theory) collected.

Found: C=62·7, H=8·4%; calculated for $C_{14}H_{22}O_5$, C=62·2, H=8·1%.

The boiling point at 12 mm. was found to be 178–179°. Openshaw and Robinson (*loc. cit.*) quote it as 184–185°/13 mm.

Cyclohexanone-2-β-propionic acid (*X*).

The hydrolysis of the above described ester (200 g.) was effected by refluxing with a solution of hydrochloric acid (500 c.c.) in water (350 c.c.) for 12 hours. The cooled liquid was saturated with ammonium sulphate and extracted with ether, the ketonic acid being recovered from this solvent after washing and drying. It formed a brown oil (120 g.) which could be induced to crystallise on cooling, but was distilled under reduced pressure. The main fraction, a colourless oil boiling at 183–4°/12 mm. solidified completely on cooling. Recrystallised from petroleum ether it was obtained in radiating clusters of small white needles, m.p. 62°.

Found: C=63·7, H=8·2%; calculated for $C_9H_{14}O_3$, C=63·5, H=8·2%.

When melted and allowed to resolidify this acid has a characteristic waxy appearance. It has a definite faint odour recalling hawthorn. Treatment of a hot aqueous alkaline solution of the acid with semicarbazide for 30 minutes, followed by careful acidification leads to formation of the *semicarbazone* which on recrystallisation from methyl alcohol is obtained in small clusters of hard white prisms melting at 194° (with decomposition).

Found: N=18·4%; calculated for $C_{10}H_{17}O_3N_3$, N=18·4%.

Ethyl cyclohexanone-2-β-propionate.

The acid (X) (110 g.) was dissolved in absolute ethyl alcohol (300 c.c.), concentrated sulphuric acid (10 c.c.) added and the solution refluxed for 6 hours. After removal of excess alcohol by distillation water was added and the heavy oil taken up, washed and dried in ether, the solvent removed and the residual oil distilled *in vacuo*. A colourless mobile oil (110 g.; 80% of theory) boiling at 140–143°/12 mm. was collected.

Found: C=66·4, H=8·9%; calculated for $C_{11}H_{18}O_3$, C=66·7, H=9·1%.

Methyl cyclohexanone-2-β-propionate.

This ester was prepared by refluxing a solution of the acid (X) (16 g.) in absolute methyl alcohol (60 c.c.) containing dry hydrogen chloride (5 g.) for 5 hours. The ester was finally distilled *in vacuo* and obtained as a colourless mobile oil (13 g.) boiling at 133–4°/12 mm.

Found: C=64·9, H=8·7%; calculated for $C_{10}H_{16}O_3$, C=65·2, H=8·7%.

Cyclohexanone-2-β-propionamide (XIII).

Ethyl cyclohexanone-2-β-propionate (5 g.) was added to concentrated aqueous ammonium hydroxide solution (30 c.c. of 20E) and the mixture kept well shaken for several hours. The oil had then been converted into a mass of crystals, which were filtered off, washed with a little cold water and dried in the air (2·5 g.). After recrystallisation from ethyl alcohol in which the substance is readily soluble in the hot but only sparingly so in the cold, it was obtained in small colourless plates, m.p. 162–3°.

Found: C=63·8, H=9·0%; calculated for $C_9H_{15}O_2N$, C=63·9, H=8·9%.

2-Keto-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-octahydroquinoline (XIV).

The amide (XIII) (5 g.) was heated in a test-tube at a few degrees above its melting point for several minutes until evolution of gas had apparently ceased. On cooling the melt crystallised in very pale yellow needles, which after recrystallisation from alcohol melted at 142°.

Found: C=71·5, H=8·8%; calculated for $C_9H_{13}ON$, C=71·6, H=8·6%.

5-Carboxy-1 : 2 : 3 : 4-tetrahydroacridine-1-β-propionic acid (XI).

The acid (X) was added to a solution of isatin (9 g.) and potassium hydroxide (20 g.) in water (50 c.c.) and the solution heated at 100° for 8 hours. The red-brown liquid was then diluted with an equal volume of water, boiled with charcoal and after filtration and cooling, acidified with acetic acid and allowed to stand. Small yellow prisms soon commenced to separate, and after standing overnight they were collected and thoroughly washed with water. The acid so obtained is not very soluble in any of the usual organic solvents though it does dissolve in much acetic acid and is somewhat soluble in hot nitrobenzene. For analysis it was taken up in alkali and reprecipitated with acetic acid and then thoroughly washed with water. The very small pale yellow prisms thus obtained melted at 307–8° (with decomposition).

Found : $C=68{\cdot}0$, $H=5{\cdot}8\%$; calculated for $C_{17}H_{17}O_4N$, $C=68{\cdot}2$, $H=5{\cdot}7\%$.

1 : 2 : 3 : 4-Tetrahydroacridine-1-β-propionic acid (XII).

Decarboxylation of the acid (XI) to 1 : 2 : 3 : 4-tetrahydroacridine-1-β-propionic acid was not easy to accomplish. In one experiment it was found possible to extract a small amount of alkali soluble material from the cooled melt obtained by heating the acid (XI) above its melting point (at about 310°) until decomposition was apparently complete. Treatment of the alkaline extract with charcoal followed by filtration and acidification with acetic acid led to precipitation of a brown powder, somewhat soluble in ether and in ethyl acetate. Recrystallised from aqueous methyl alcohol it was obtained in yellowish brown needles melting at 164–165°.

Found : $C=74{\cdot}7$, $H=6{\cdot}7\%$; calculated for $C_{16}H_{17}O_2N$, $C=75{\cdot}3$, $H=6{\cdot}6\%$.

That this substance was actually 1 : 2 : 3 : 4-tetrahydroacridine-1-β-propionic acid (XII) was shown by this analysis, the melting point, and the fact that the melting point was not depressed when the substance was admixed with some of the acid prepared from o-amino benzaldehyde as described below. However, the yield in this experiment was quite small, and usually the only product of decarboxylation was a dark brown oil quite insoluble in alkali. This became very thick on cooling but could not be induced to crystallise. It did not dissolve completely in ether, but the ethereal solution, which showed a very intense beautiful green fluorescence, deposited a heavy golden yellow oil on concentration. An alcoholic solution of this oil reacted with picric acid and an oily picrate was deposited. This could not be induced to crystallise. Treatment of the oil with excess methyl iodide under pressure at 100° led to formation of an oily brown *methiodide.*

Ethyl 5-carboxy-1 : 2 : 3 : 4-tetrahydroacridine-1-β-propionate.

The dicarboxylic acid (XI) (6 g.) was dissolved in absolute ethyl alcohol (60 c.c.) and concentrated sulphuric acid (8 g.) added. The solution was then refluxed for 6 hours, most of the alcohol was removed by evaporation, and the residue diluted with water and made just alkaline with ammonia. Decolourising charcoal was added and after thorough agitation the liquid was filtered. The pale yellow clear filtrate was carefully acidified and allowed to stand. The ester gradually crystallised in beautiful colourless prisms. It was recrystallised from hot water and obtained in colourless small prisms, which melt at 100° with loss of water, then resolidify and finally melt at 174°.

Found: $C=68{\cdot}2$, $H=6{\cdot}6$, $N=4{\cdot}3\%$; calculated for $2C_{19}H_{21}O_4N, H_2O$, $C=67{\cdot}9$, $H=6{\cdot}6$, $N=4{\cdot}2\%$.

The substance is thus a hydrate. After heating at 100° for about 2 hours some resolidified material (3 g.) was collected and heated in a test-tube in an oil-bath. The solid melted, and commenced to evolve CO_2 at about 210°. The temperature was gradually raised and finally maintained at 240° for 15 minutes. The brown liquid was then allowed to cool, and was at once hydrolysed with alcoholic potash under reflux for 3 hours. After removal of alcohol and addition of water, the liquid was extracted with ether, then treated with charcoal, filtered and carefully acidified with acetic acid. Light brown crystals of 1 : 2 : 3 : 4-tetrahydroacridine-1-β-propionic acid melting at 164° alone or admixed with authentic material were obtained.

Some preliminary attempts to effect the condensation of ethyl cyclohexanone-2-β-propionate with o-aminobenzaldehyde in presence of piperidine (cf. Stark, *Berichte*, 1907, *40*, 3427; Stark and Hoffman, *ibid.*, 1909, *42*, 715) were unsuccessful. Better results were obtained by the following method: Ethyl cyclohexanone-2-β-propionate (10 g.) and o-aminobenzaldehyde (6 g.) were dissolved in ethyl alcohol (40 c.c.) and a solution of sodium hydroxide (5 g.) in water (20 c.c.) added. The mixture was then allowed to stand at room temperature for 15 days. It was freed from a small amount of yellow material by filtration, diluted with water and the alcohol boiled off, heated with charcoal, filtered and acidified with acetic acid. A yellow oil was thrown out, which soon crystallised. After recrystallisation from aqueous methyl alcohol it was obtained in fine yellow needles melting at 164–165° (11·2 g.; 75% of theory).

Found: C=75·0, H=6·7%; calculated for $C_{16}H_{17}O_2N$, C=75·3, H=6·6%.

Ethyl 1 : 2 : 3 : 4-tetrahydrocarbazolenine-11-β-propionate (*XV*).

A mixture of ethyl cyclohexanone-2-β-propionate (9·9 g.) and phenylhydrazine (5·4 g.) rapidly turned milky owing to separation of water, and evolved heat. On one occasion such a mixture became crystalline on allowing to stand but the crystals could not be purified and rapidly changed to a brown oil. Usually after warming on the water-bath for a few minutes glacial acetic acid (50 c.c.) was added and the solution gently refluxed for 2 hours. The resultant greenish solution was poured into water and the separated oil taken up in ether, freed of acetic acid by washing with sodium bicarbonate solution, dried, and the solvent removed. A dark green oil (13 g.; yield practically quantitative), completely soluble in dilute hydrochloric acid, remained. It was distilled *in vacuo* and a fraction boiling at 225–8°/15 mm. was collected. The carbazolenine ester thus obtained was a thick pale yellow oil. On exposure to air it gradually became a pure olive green in colour, the surface layers first changing colour. Continued exposure caused the colour to change eventually to dirty brown.

Found: C=74·9, H=7·9%; calculated for $C_{17}H_{21}O_2N$, C=75·3, H=7·8%.

Treatment of this carbazolenine ester (5 g.) with methyl iodide (15 g.; excess) in a sealed tube at 100° for 90 minutes led to formation of the methiodide, which was obtained as a brown gum after removal of excess methyl iodide. It was purified by repeated recrystallisation from a mixture of methyl alcohol and ethyl acetate and obtained in magnificent pale yellow prisms, m.p. 165°.

Found: C=52·1, H=5·9, I=30·4%; calculated for $C_{18}H_{24}O_2NI$, C=52·3, H=5·8, I=30·7%.

1 : 2 : 3 : 4-Tetrahydrocarbazolenine-11-β-propionic acid.

Hydrolysis of the ester (XV) with boiling alcoholic potash for 3 hours followed by removal of the alcohol, dilution with water, decolourisation with charcoal, filtration and acidification with acetic acid, led to precipitation of the carbazolenine acid as a sandy powder. After several recrystallisations from methyl alcohol it was obtained in colourless prisms, m.p. 226° (in agreement with Openshaw and Robinson, *loc. cit.*).

Found: C=74·0, H=7·2%; calculated for $C_{15}H_{17}O_2N$, C=74·1, H=7·0%.

11-Ethyl-1 : 2 : 3 : 4-tetrahydrocarbazolenine (*XIX*) *and 1-Ethyl-1 : 2 : 3 : 4-tetrahydrocarbazole* (*XX*).

2-Ethylcyclohexanone (12·6 g.) and phenylhydrazine (11 g.) were warmed together on the water-bath. Water soon separated and the mixture became yellow. The oily phenylhydrazone was dissolved in glacial acetic acid (150 c.c.) and the solution gently refluxed for 2 hours, after which it was poured into water, basified with ammonia and extracted several times with ether. The combined ethereal extracts were treated with dilute hydrochloric acid, then washed with water, dried and the solvent removed. The small quantity of residual oil was distilled *in vacuo*, 2 grams of a pale yellow viscous oil boiling at 200–205°/16 mm. being collected. This substance was the tetrahydrocarbazole (XX).

Found: C=84·1, H=8·6%; calculated for $C_{14}H_{17}N$, C=84·4, H=8·5%.

The hydrochloric acid extract of the original ether solution was made alkaline and the oil which separated taken up, washed and dried in ether, and the solvent removed. The residual oil was distilled *in vacuo*, a pale yellow viscous oil (15 g.) boiling at 160–161°/16 mm. being collected. The basic character of this oil and its analysis prove it to be the carbazolenine (XIX).

Found: C=84·2, H=8·7%; calculated for $C_{14}H_{17}N$, C=84·4, H=8·5%.

This base dissolves readily in acids. Its *picrate* is readily obtained by mixing alcoholic solutions of picric acid and of the base and after recrystallisation from alcohol melts at 147°.

Found: N=13·4%; calculated for $C_{20}H_{20}O_7N_4$, N=13·1%.

Methiodides of 11-ethyl-1 : 2 : 3 : 4-tetrahydrocarbazolenine.

11-Ethyl-1 : 2 : 3 : 4-tetrahydrocarbazolenine (5 g.) was dissolved in methyl iodide (20 g.; excess) and heated in a sealed tube at 100° for 15 minutes. The base had been completely converted to crystalline methiodide by that time. It was taken up in hot alcohol and benzene was added to the filtered hot solution. Yellowish prisms commenced to separate almost immediately but when the solution had cooled the solid was orange-red in colour. If it was now taken up in methyl alcohol, in which it is very soluble, a yellow solution was obtained, and on adding ethyl acetate to the hot solution, evaporating somewhat, cooling and scratching, almost colourless crystals deposited. However, after a few minutes the red form appeared and agitation soon led to disappearance of the yellow form, all the solid being the red form. Eventually it was found possible to isolate the pale yellow form in quite well formed rhombic tablets by careful dilution of a hot methyl alcoholic solution with ethyl acetate. The pale yellow form melted at 153°.

Found: C=52·5, H=5·8, N=4·3%; calculated for $C_{15}H_{20}NI$, C=52·8, H=5·9, N=3·7%.

The red form melts at 94°.

Found: C=52·6, H=5·7, N=4·4%; calculated for $C_{15}H_{20}NI$, C=52·8, H=5·9, N=3·7%.

Ethiodide of 11-ethyl-1 : 2 : 3 : 4-tetrahydrocarbazolenine.

The base (XIX) (5 g.) and ethyl iodide (20 g.; excess) were heated together under reflux for 2 hours. Solid commenced to separate almost immediately. The ethyl iodide was evaporated and the solid was washed with cold ethyl acetate in which it is slightly soluble. Finally it was recrystallised from a mixture of ethyl alcohol and benzene and obtained pure in almost colourless prisms, m.p. 192°.

Found: C=53·7, H=6·0, N=4·3%; calculated for $C_{16}H_{22}NI$, C=54·1, H=6·2, N=4·0%.

ACKNOWLEDGMENT.

In conclusion the author desires to express his gratitude to Professor R. Robinson, F.R.S., for having suggested this work and for many helpful suggestions.

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THE SYNTHESIS OF 2-AMINOMETHYL—BENZIMINAZOLE AND RELATED SUBSTANCES.

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and Francis Lions, B.Sc., Ph.D.

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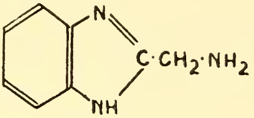
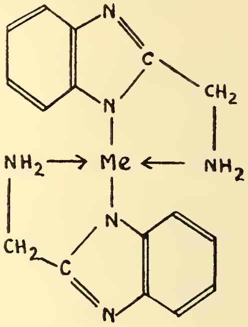
Several unsymmetrically substituted ethylene diamines with molecules possessing at least one plane of symmetry have been used in recent years in the investigation of the stereochemistry of coordination compounds, notably of the 4-covalent metals such as nickel, platinum and palladium. Thus, for example, Reihlen and Hühn (*Annalen*, 1931, *489*, 42 ; 1932, *499*, 144 ; 1935, *519*, 80) have prepared 1 : 2-isobutylene diamine and 2-aminomethyl-3-methyl-4-ethyl quinoline and examined the coordination complexes formed by these bases with platinum and palladium. A good review of this subject by Bailar is available in *Chemical Reviews*, 1936, *19*, 67–87.

It appeared to the authors that 2-aminomethyl benziminazole (I) might prove worthy of investigation as a base for the study of coordination problems, because the imino hydrogen of the benziminazole nucleus is capable of being replaced by metals, as was first shown by Bamberger and Lorenzen (*Annalen*, 1893, *273*, 271–279). Stable metallic complex compounds in which a central bivalent metallic element is bound to two aminomethyl benziminazole nuclei by two electrovalencies and two coordination covalencies, as in (II), should thus be obtainable. These substances should still possess basic properties by virtue of the two basic nitrogen atoms in the three positions of the iminazole nuclei, so that salt formation with acids ought readily to occur ; and where there is a tetrahedral disposition of the four valencies of the central metallic atom, it should be possible to effect resolution of the complex by salt formation with optically active acids and fractionation in the usual way. Such a salt formation process followed by elimination of the active acid half ought not to disturb the disposition of the group about the central metallic atom. It should be remembered, however, that e.g. the dihydrochloride of the complex (I) might be formulated equally well as (II) or (III)—between which formulæ it would probably be difficult to distinguish chemically.



I.



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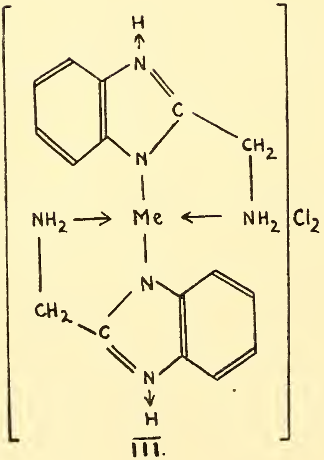

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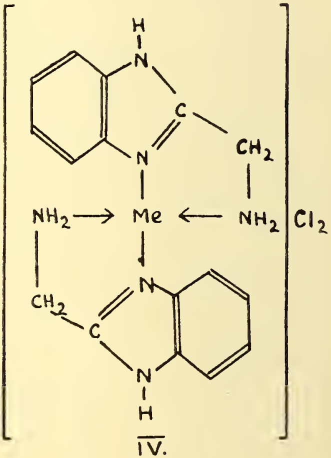
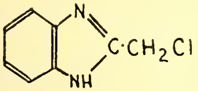


IV.

We have found the synthesis of 2-aminomethyl benziminazole not easy. Glycine could not be made to condense with o-phenylenediamine by heating the components together or by refluxing them together in 4N hydrochloric acid solution (cf. Phillips, *J.C.S.*, 1928, 2393). A method was then worked out for the preparation of

2-chloromethyl benziminazole (V) in quantity. It was found possible to obtain (V) by boiling a solution of o-phenylenediamine and chloracetic acid in 4N hydrochloric acid, but the yield was not good and the product was difficult to purify. A better method was to obtain 2-hydroxymethyl benziminazole by Phillips's method (*loc. cit.*) and by treatment of this with thionyl chloride to prepare the hydrochloride of (V). Careful basification with sodium carbonate solution then liberated the free base, a colourless crystalline substance with a very reactive chlorine atom. Alkalies react at once with this chlorine but it is impossible to isolate homogeneous products from the reaction mixtures. Also, just above its melting point the substance passes at once to a solid red brown resin. As is to be expected the base (V) is a lachrymator and also possesses sternutatory properties. Attempts to replace the chlorine atom by an $-NH_2$ group all proved abortive. Reaction with either aqueous or alcoholic ammonia is quite complex, several substances being formed, but apparently none of the required base (I), and we reserve discussion of this reaction for the present.



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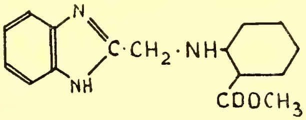

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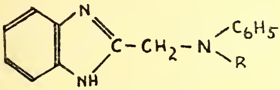
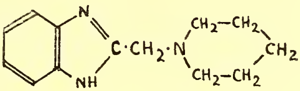
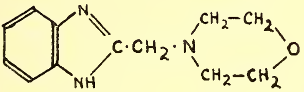


(R = CH_3, C_6H_5)

VII.



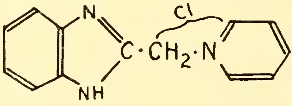
VIII.



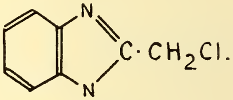
IX.

In view of this failure, the reaction of 2-chloromethyl benziminazole with bases was then studied. It was found that reaction occurred very readily, but only with secondary amines could the expected products be easily isolated. Primary amines such as aniline, p-toluidine and m-nitraniline all gave products similar to those obtained from ammonia. Curiously enough, methyl anthranilate did react to give the expected product, 2-o-carbomethoxy-anilinomethylbenziminazole (VI). It will be recalled that methyl anthranilate fails to behave as a primary aromatic amine in the Paal-Knorr pyrrole synthesis (cf. Hazlewood, Hughes and Lions, *Journ. and Proc. Roy. Soc. N.S.W.*, 1937, *71*, 92). Secondary bases such as methylaniline, diphenylamine, piperidine, and morpholine reacted readily with (V) to give the expected ditertiary bases (VII), (VIII) and (IX).

Heating of a solution of (V) in dry pyridine leads to a sudden violent reaction and precipitation of a white solid which is probably the quaternary salt (X).



X.

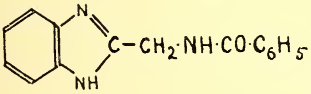


XI.

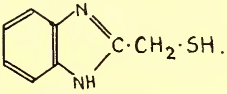
It was thought that methylation of the imino group of the benziminazole nucleus might conceivably affect the course of reaction of an attached 2-chloromethyl group with ammonia and primary amines. Hence, 2-hydroxymethyl benziminazole was methylated to 1-methyl-2-hydroxymethyl benziminazole and this was converted by means of thionyl chloride to 1-methyl-2-chloromethyl benziminazole (XI). Again, the reaction of this substance with ammonia was complex ; but it was possible to isolate 1-methyl-2-anilinomethyl benziminazole from the reaction of (XI) with aniline ; and methyl aniline reacted normally to give 1-methyl-2-methylanilino methyl benziminazole.

The failure to obtain 2-anilinomethyl benziminazole (XII) from the reaction of (V) with aniline led to attempts to prepare this substance from o-phenylene diamine and phenylglycine. No success was achieved using the method of Phillips, but (XII) was obtained by careful fusion together of the two components. This success suggested that it should be possible to condense o-phenylene diamine with a derivative of glycine such as phthalimidoacetic acid or hippuric acid in which the basicity of the glycine

$-NH_2$ group has been depressed by acylation. The resulting products should be capable of hydrolysis to the required base (I). Experiment showed that condensation of phthalimidoacetic acid with o-phenylenediamine could be brought about either by Phillips's method or by fusion together of the components. By the first method only a small amount of product was obtained, but by the latter method the yield was larger. The product of reaction was a white amorphous infusible base, soluble in acids but insoluble in the usual organic solvents. Analysis indicated complete absence of oxygen and we cannot ascribe a structural formula to it. Hippuric acid could not be condensed with o-phenylene diamine by Phillips's method, but fusion of equimolecular quantities of o-phenylenediamine and hippuric acid led to ready formation of 2-benzoylamino methyl benziminazole (XIII) in good yield. Refluxing this substance with concentrated hydrochloric acid for five hours leads to extrusion of the benzoyl group and formation of the dihydrochloride of (I). The conversion of this substance to the base afforded some difficulty until a full knowledge of the process was obtained. The dihydrochloride crystallises with a molecule of water of crystallisation but this can be removed by heating at 110°. Treatment of this dehydrated salt with a solution of sodium methoxide in dry methanol for some time led to precipitation of sodium chloride, which was filtered off. The filtrate was evaporated *in vacuo* and the base obtained as a gum which could not be distilled, or induced to crystallise. It is very soluble in water, and could not apparently be recrystallised from this solvent. Eventually, however, it was found possible to crystallise out a low melting hydrate from the aqueous solution, and it is readily possible to obtain this hydrate by decomposition of the dihydrochloride in fairly concentrated aqueous solution with alkali, followed by seeding. This base readily coordinates with metallic ions, such as copper in copper sulphate and a complete account of these substances will be published later.

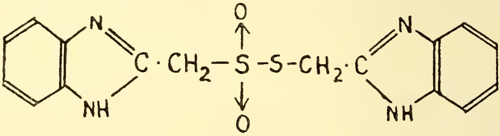


XIII.



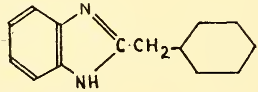
XIV.

It also appeared worth while to prepare 2-sulphydryl methyl benziminazole (XIV) and to examine its tendency to form coordination compounds with metallic salts. Thioglycollic acid was found to condense readily with o-phenylene diamine in hot 4N hydrochloric acid solution, and the thiol (XIV) was readily isolated as a white crystalline compound, which is very sensitive to oxidation. It does coordinate with metals such as nickel and copper, but the products are very difficult to work with, and seem to eliminate metallic sulphide with great ease. Passage of air through an ammoniacal solution of (XIV) is sufficient to oxidise it to a compound $C_{16}H_{14}O_2N_4S_2$, which is probably the disulphoxide (XV). The same substance is also obtained by oxidation of (XIV) with dilute nitric acid.

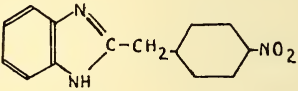


XV.

Finally, the preparation is recorded of a series of 2-substituted benziminazoles from o-phenylene diamine, using the method of Phillips. Phenylacetic acid and o- and p-nitrophenylacetic acids in particular were converted to 2-benzyl benziminazole (XVI) 2-o-nitrobenzyl benziminazole (XVII) and 2-p-nitrobenzyl benziminazole (XVIII).



XVI.



XVIII.

The methylene group of these compounds should be reactive, and the reactivity should be enhanced by methylation of the nitrogens of the benziminazole nucleus. The result of investigation of these properties will be reported later.

Experimental.

2-Chloromethyl benziminazole (*V*).

(*a*) A solution of o-phenylene diamine (22 g. ; 0·2 mol.) and chloracetic acid (20 g. ; slightly more than 0·3 mol.)

in hydrochloric acid (200 c.c. of 4N) was boiled under reflux for 40 minutes. The colour changed from red through yellow to green during the heating. After filtration and allowing to cool, the solution was carefully basified with sodium carbonate solution and the white solid which separated was well washed, then recrystallised from dilute alcohol. For analysis it was twice recrystallised from a mixture of alcohol and ethyl acetate and thus obtained in colourless needles melting at 160–161°.

Found: C=57·4, H=4·1, N=18·3%; calculated for $C_8H_7N_2Cl$, C=57·7, H=4·2, N=18·1%.

(*b*) A better method of preparation was as follows: 2-hydroxymethyl benziminazole was prepared in 71% yield according to the method of Phillips (*loc. cit.*). To this base (95 g.) was gradually added a solution of thionyl chloride (140 c.c.) in chloroform (200 c.c.) and finally the mixture was heated on the water-bath under reflux for two hours. Excess thionyl chloride and chloroform were then removed by distillation *in vacuo*, and the cooled residual solid mass was dissolved in water, the solution cooled to 0° and carefully basified with ice-cold sodium carbonate solution. The precipitated solid was quickly filtered and washed free from alkali, then dried in a vacuum desiccator (94 g.). The product was purified by recrystallisation from ethyl acetate, m.p. 160–161°, alone or admixed with material as prepared above.

2-Chloromethyl benziminazole is insoluble in water, benzene, ether, and petroleum ether. It dissolves readily in methyl and ethyl alcohols, and can be obtained in large needles by slow evaporation of the alcoholic solution. It has a very irritating effect on the skin and any mucous membranes, and causes sneezing.

Attempts were made to replace the chlorine atom with an $-NH_2$ group, using various modifications of the following conditions:

(*a*) Addition of an alcoholic solution of the chloromethyl base (V) to a large excess of saturated alcoholic ammonia solution;

(*b*) addition of an alcoholic solution of (V) to concentrated aqueous ammonia;

(*c*) passage of a rapid stream of ammonia into an alcoholic solution of the base (V);

(*d*) shaking the solid (V) with concentrated aqueous ammonia solution.

In all the experiments a mixture of substances was obtained which could be separated partially by recrystallisation from various solvents. All the solid products obtained have high melting points and seem to be chain compounds.

The base (V) reacts in a similar way to give high melting compounds with aniline, p-toluidine, m-nitraniline, sodium acetate, and potassium phthalimide. On heating a few degrees above its melting point it suddenly solidifies to a red resin with evolution of heat.

Substituted 2-aminomethyl benziminazoles could be prepared from (V) and methyl anthranilate or secondary bases by the following method: a solution in alcohol (10 c.c.) of the base (V) (2 g.) and slightly more than the theoretical amount of amine was gently refluxed for 30 minutes. After cooling, the solution was poured into water and ammonia added. The precipitated product was collected and recrystallised. The yields were usually good for secondary amines.

2-o-Carbomethoxyanilino methyl benziminazole (VI).

From (V) and methyl anthranilate. Very pale yellow needles m.p. 216° from alcohol.

Found: N=15·1%; calculated for $C_{16}H_{17}O_2N_3$, N=14·9%.

2-Methylanilino methyl benziminazole (VII, $R=CH_3$).

From (V) and methyl aniline. Very pale yellow needles, m.p. 202°, from aqueous alcohol.

Found: N=18·1%; calculated for $C_{15}H_{15}N_3$, N=17·8%.

2-Diphenylamino methyl benziminazole (VII, $R=C_6H_5$).

From (V) and diphenylamine. Colourless needles, m.p. 215°, from aqueous alcohol.

Found: N=14·8%; calculated for $C_{20}H_{17}N_3$, N=14·5%.

2-Piperidino methyl benziminazole (VIII).

From (V) and piperidine. Colourless prisms melting at 193–4° (with previous softening at 180°) from ethyl acetate or aqueous alcohol.

Found: N=19·4%; calculated for $C_{13}H_{17}N_3$, N=19·5%.

2-Morpholino methyl benziminazole (*IX*).

From (V) and morpholine. Long needles (colourless), m.p. 211°, from water.

Found: N=19·4%; calculated for $C_{12}H_{15}ON_3$, N= 19·4%.

1-Methyl-2-hydroxymethyl benziminazole.

2-Hydroxymethyl benziminazole (14·8 g.) was dissolved in the minimum amount of methyl alcohol and then dimethyl sulphate (9·5 c.c.) and a solution of sodium hydroxide (4 g.) in water (12 c.c.) added alternately in small portions. Heat was evolved during the additions. The mixture was finally heated to 100° for 10 minutes and poured into water after cooling. The precipitate was well washed with water and was then recrystallised from hot water, being obtained in beautiful long flat needles, m.p. 105°.

Found: N=15·7%; calculated for $C_9H_{10}O_2N$, H_2O, N=15·6%.

Dried at 100° for several hours the substance lost water. The melting point rose to 143–144°. A fresh analysis showed N=17·0%; calculated for $C_9H_{10}ON_2$, N=17·1%.

1-Methyl-2-chloromethyl benziminazole (*XI*).

This substance was prepared from the above described 1-methyl-2-hydroxymethyl benziminazole by the help of thionyl chloride exactly as the compound (V) was prepared from 2-hydroxymethyl benziminazole. It was eventually recrystallised from a benzene-petroleum ether mixture and obtained in fine colourless prisms, m.p. 94°.

Found: N=15·3%; calculated for $C_9H_9N_2Cl$, N= 15·5%.

This substance still retained some of the irritant properties of the unmethylated compound. The decrease in melting point and increase in solubility in non-aqueous solvents caused by the introduction of the methyl group is also noteworthy. Presumably the polarity between the two nitrogen atoms of the benziminazole nucleus is considerably decreased on methylation.

The reaction of this chloromethyl compound (XI) with ammonia was apparently complex. Various experimental conditions were tried but it was not possible to isolate 1-methyl-2-amino methyl benziminazole from any of the reaction mixtures.

1-Methyl-2-anilino methyl benziminazole.

Treatment of (XI) (2 g.) in alcohol (10 c.c.) with a slight excess of aniline at the boiling point led to formation of 1-methyl-2-anilino methyl benziminazole which could be obtained from aqueous alcohol in colourless needles, m.p. 118°.

Found: N=18·0%; calculated for $C_{15}H_{15}N_3$, N=17·7%.

1-Methyl-2-methylanilino methyl benziminazole.

This substance was obtained by heating (XI) (2 g.) in alcohol (10 c.c.) with a slight excess of methyl aniline, and working up the product in the usual way. It was obtained in fine colourless needles, m.p. 145°, from aqueous alcohol.

Found: N=17·0%; calculated for $C_{16}H_{17}N_3$, N=16·7%.

2-Anilino methyl benziminazole.

Phenylglycine (3 g.) and o-phenylene diamine (2 g.) were finely ground, intimately mixed and then carefully melted together. When the melt was uniform the temperature was increased until water was evolved and the heating was continued for about three minutes longer. During the heating the colour changed through brown and green to blue. After cooling the mass was powdered and dissolved in dilute hydrochloric acid; the solution was decolourised with charcoal, filtered and made alkaline with ammonia. The precipitated solid was recrystallised from aqueous alcohol and obtained in colourless needles, m.p. 162°.

Found: N=18·5%; calculated for $C_{14}H_{13}N_3$, N=18·8%.

Condensation of o-Phenylene Diamine and Phthalimidoacetic acid.

Fusion together of equimolecular quantities of o-phenylene diamine and phthalimidoacetic acid gave a purple product which was taken up in dilute hydrochloric acid, and finally precipitated as a white amorphous mass by ammonia. It was insoluble in any of the usual organic solvents and was infusible. A carefully washed and dried sample was analysed.

Found: C=75·7, H=6·1, N=17·8%.

There is thus apparently no oxygen present and it is difficult to devise a structural formula.

2-Benzoylamino methyl benziminazole (*XIII*).

Equimolecular quantities of o-phenylene diamine and hippuric acid were finely ground and intimately mixed, then carefully fused. The temperature was then raised to 160°, when water was evolved. The melt changed colour from brown through green to a brilliant blue with a red fluorescence. After cooling the glassy mass was powdered and dissolved at moderate temperature in the minimum of dilute hydrochloric acid, treated with charcoal to remove the material responsible for the intense colours, and then precipitated with ammonia. The precipitate was filtered and recrystallised from dilute alcohol (70%) and obtained in colourless feathery needles, m.p. 231°. The yield was excellent.

Found: N=15·4%; calculated for $C_{15}H_{13}ON_3,H_2O$, N=15·6%.

If recrystallised from absolute alcohol the substance is obtained in small octahedra, m.p. 231°.

Found: N=17·0%; calculated for $C_{15}H_{13}ON_3$, N=16·7%.

Admixture of the two materials caused no depression of melting point, the hydrated form probably losing water and passing over to the anhydrous form during the heating.

2-Aminomethyl benziminazole dihydrochloride.

2-Benzoylamino methyl benziminazole (33 g.) was heated under reflux with concentrated hydrochloric acid (75 c.c.) for five hours. After cooling, and addition of a little water the precipitated benzoic acid was filtered off and the filtrate evaporated to dryness *in vacuo*. The crystalline residue was only slightly soluble in alcohol. It was freed from traces of benzoic acid by successive extractions with hot alcohol, and was finally recrystallised from much alcohol.

Found: C=40·2, H=6·1, N=17·2, Cl=30·3%; calculated for $C_8H_9N_3,2HCl,H_2O$, C=40·3, H=5·5, N=17·6, Cl=30·0%.

The salt could be freed from water of crystallisation by heating at 110° for some time. The anhydrous salt melts at 263°.

2-Aminomethyl benziminazole (*I*).

After preliminary attempts to isolate the base in anhydrous form, which gave only brown gums, readily soluble in alcohol and water but not in ether or benzene, it was found quite easy to isolate the base as a hydrate, m.p. 53°, by treatment of the concentrated aqueous solution of its hydrochloride with just sufficient sodium carbonate solution. The hydrate crystallised out in a mass of feathery needles and could be readily recrystallised from water.

Found : $C = 47{\cdot}9$, $H = 7{\cdot}4$, $N = 21{\cdot}1\%$; calculated for $C_8H_9N_3, 3H_2O$, $C = 48{\cdot}3$, $H = 7{\cdot}7$, $N = 20{\cdot}9\%$

Attempts to dry this substance in a vacuum over concentrated sulphuric acid led to loss of water, but the crystals rapidly coalesced to a gum.

2-Acetylamino methyl benziminazole.

Treatment of dilute aqueous solution of the base (I) with acetic anhydride in slight excess leads to rapid acetylation and precipitation of the 2-acetylamino compound, which was obtained in magnificent colourless needles after recrystallisation from water ; m.p. 200°.

Found : $N = 22{\cdot}4\%$; calculated for $C_{10}H_{11}ON_3$, $N = 22{\cdot}2\%$.

2-Sulphydryl methyl benziminazole (XIV).

Thioglycollic acid and o-phenylene diamine (50 g.) were dissolved in 4N hydrochloric acid (500 c.c.) and heated under reflux for 60 minutes. After cooling the solution was quickly basified with ammonia and the precipitated solid at once filtered, washed with water and recrystallised from aqueous alcohol. Colourless prisms (50 g.) melting at 158° were obtained.

Found : $N = 16{\cdot}9\%$; calculated for $C_8H_8N_2S$, $N = 17{\cdot}1\%$.

On evaporating the mother liquors from the recrystallisation of (XIV) a colourless crystalline substance melting at 182° was isolated in white feathery needles after recrystallisation from alcohol. It could also be obtained by passing air through an ammoniacal alcoholic solution of (XIV), or by treating (XIV) with dilute nitric acid under very carefully controlled conditions.

Found : $N = 15{\cdot}7\%$; calculated for $C_{16}H_{14}N_4O_2S_2$, $N = 15{\cdot}6\%$.

This substance is probably the disulphoxide (XV).

Preparation of 2-substituted benziminazoles.

For the preparation of the following substances the method used was essentially that of Phillips (*loc. cit.*)

except that the time of refluxing was increased to approximately two hours. In each experiment the original red colour of the hydrochloric acid solution changed to green during the course of the reaction. The yield of crude bases varied between 50 and 60%.

2-Phenoxymethyl benziminazole.

From phenoxyacetic acid and o-phenylene diamine. White needles, m.p. 162°, from aqueous alcohol.

Found: N=12·6%; calculated for $C_{14}H_{12}ON_2$, N=12·5%.

2-Methoxy methyl benziminazole.

From methoxyacetic acid and o-phenylene diamine. Pale yellow plates, m.p. 136°, from aqueous alcohol.

Found: N=17·4%; calculated for $C_9H_{10}ON_2$, N=17·3%.

2-Benzyl benziminazole (*XVI*).

From phenylacetic acid and o-phenylene diamine. Slender colourless needles, m.p. 187°, from alcohol. This substance has been previously prepared by Walther and v. Pulawski (*J. pr. Chem.*, (2), *59*, 253) by heating phenylacetic acid with o-phenylene diamine at 180°.

2-β-Phenylethyl benziminazole.

From β-phenyl propionic acid and o-phenylene diamine. Colourless needles, m.p. 186°, from ethyl acetate.

Found: N=12·5%; calculated for $C_{15}H_{14}N_2$, N=12·6%.

2-p-Nitrobenzyl benziminazole (*XVIII*).

From p-nitrophenylacetic acid and o-phenylene diamine. Pale yellow needles, m.p. 215°, from aqueous alcohol.

Found: N=16·3%; calculated for $C_{14}H_{11}O_2N_3$, N=16·6%.

2-o-Nitrobenzyl benziminazole (*XVII*).

From o-nitrophenylacetic acid and o-phenylene diamine. Pale yellow needles, m.p. 217°, from aqueous alcohol.

Found: N=16·5%; calculated for $C_{14}H_{11}O_2N_3$, N=16·6%.

2-p-Aminobenzyl benziminazole.

From p-aminophenylacetic acid and o-phenylene diamine. Very pale yellow needles, m.p. 213°, from aqueous alcohol.

Found: N=19·0%; calculated for $C_{14}H_{13}N_3$, N=19·3%.

ACKNOWLEDGMENT.

The authors desire to express their grateful acknowledgment to Miss E. Goulston, B.Sc., for some of the analyses recorded in this paper.

Department of Organic Chemistry,
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ON THE CHEMISTRY OF THE REACTION OF CREATININE WITH 3, 5-DI-NITRO-BENZOIC ACID.

By Adolph Bolliger, Ph.D.

(*Manuscript received, September 14, 1937. Read, October 6, 1937.*)

Last year it was reported that creatinine with 3-5-di-nitro-benzoic acid in an alkaline medium gives a purple colour reaction (Bolliger, This Journal, 1935 (1936), *69*, 224). Shortly afterwards this observation was confirmed independently by Benedict and Behre (*J. Biol. Chem.*, 1936, *114*, 515) and Langley and Evans (*J. Biol. Chem.*, 1936, *115*, 333). It has been pointed out that this new reaction for creatinine is probably of a similar nature to that with picric acid, the so-called Jaffe reaction. Therefore the reaction of creatinine with di-nitro-benzoic acid was examined in a similar manner to that with picric acid (Bolliger, This Journal, 1937, *71*, 60). As in the case of the investigation of Jaffe's reaction, aqueous solutions of creatinine sodium hydroxide (Bolliger, This Journal, 1937, *71*, 40) were mixed with an alcoholic solution containing an equimolecular amount of the organic acid, in this case di-nitro-benzoic acid. Then varying amounts of alcoholic sodium hydroxide were added.

On adding the alkali to this mixture, a deep purple colour appears and a precipitate is formed. But if only about half a molecule of sodium hydroxide or less is added to this mixture, then the resulting precipitate consists mainly of sodium-di-nitro-benzoate. If one adds one to three molecules of alkali, a purple compound is obtained which according to sodium and creatinine analysis, may consist of two molecules of di-nitro-benzoic acid, one of creatinine, 4·5 of sodium hydroxide, and six of water.

$\{[(C_7H_4N_2O_2)_2\text{-}C_4H_7N_3O]4NaOH\}_2NaOH,12H_2O$. Calculated: Na, 12·85%; creatinine, 13·7%. Found: Na, 12·76%; creatinine, 13·0%.

More than half of the creatinine added originally is recovered in the supernatant fluid. On adding more than three molecules of sodium hydroxide, compounds with higher sodium content are obtained. Six or more molecules of the alkali produce a purple compound consisting of two molecules of di-nitro-benzoic acid, one of creatinine, six of sodium hydroxide and four of water.

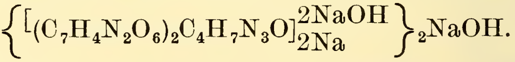
$[(C_7H_4N_2O_2)_2\text{-}C_4H_7N_2O]6NaOH,4H_2O$. Calculated: Na, 16·25%; C, 25·4%; H, 3·3. Found: Na, 16·15%; C, 25·8%; H, 3·1.

All these compounds are deep purple in colour and on heating or on exposure to air they change towards brown. They are very soluble in water, with a deep purple-red colour. But on standing, the aqueous solutions turn towards brown. They are slightly soluble in ethyl alcohol, but considerably more so in methyl alcohol. On adding silver nitrate to the aqueous solution, a voluminous gelatinous brown silver salt is obtained.

For rapid preparation of compounds of this type in a more anhydrous form, the creatinine sodium hydroxide salt was not isolated. Creatinine dissolved in varying amounts of alcoholic sodium hydroxide was mixed with equimolecular amounts of di-nitro-benzoic acid, dissolved in alcohol.

For example, on adding one millimol of creatinine dissolved in 1·9 millimols of alcoholic sodium hydroxide, of approximately normal strength to one millimol of di-nitro-benzoic acid dissolved in ten c.c. of absolute alcohol, a bright purple precipitate is obtained. After being dried *in vacuo* at 80° C., it is found to be composed of two molecules of di-nitro-benzoic acid, one of creatinine, a half molecule of sodium hydroxide, and two atoms of sodium. $\{[(C_7H_4N_2O_6)_2C_4H_7N_3O]2Na\}_2NaOH$. Calculated: Na, 9·6%; C, 35·82%; H, 2·6%; N, 16·2%. Found: Na, 9·3%; C, 36·08%; H, 3·0%; N, 16·3%.

Again, on adding more sodium hydroxide, compounds were obtained with a higher sodium content. In three experiments, using 2·31, 4 and 5 millimols of sodium hydroxide and employing absolute alcohol as a solvent, a compound was obtained which contained sodium and nitrogen in a ratio of 3·5 : 7. The analytical figures obtained agree best with the following formula:



$$\left\{[(C_7H_4N_2O_6)_2C_4H_7N_3O]^{2NaOH}_{2Na}\right\}_2NaOH.$$

Calculated: Na, 12·2%; N, 14·85%. Found: Na, 12·3%; N, 14·90%.

Using 96% alcohol as a solvent and, for example, 3·5 or 7 millimol of sodium hydroxide, a compound is obtained which contains 4·5 atoms of sodium for 7 atoms of nitrogen. The analytical figures obtained would suggest the following formula:

$$\left\{[(C_7H_4N_2O_6)_2C_4H_7N_3O]^{2NaOH}_{2Na}\right\}_2NaOH.$$

Calculated: Na, 15·15%; N, 14·35%. Found: Na, 15·00%; N, 14·56%.

These compounds resemble those obtained by the previous method, where the creatinine sodium hydroxide was isolated beforehand.

COMPOUND A.

After these preliminary investigations, about 10 gm. of one particular compound were prepared, which in future shall be called Compound A. On this occasion, two molecules of di-nitro-benzoic acid were added to one molecule of creatinine, because it had been observed in the previous experiments that these compounds occur in this proportion. Absolute alcohol was used and the creatinine was dissolved in three molecules of alcoholic sodium hydroxide. Under these circumstances Compound A is obtained as a bright purple crystalline powder at a yield of about 85%. In the supernatant fluid is found a very little excess of free alkali. If four molecules of sodium hydroxide are added, Compound A again is obtained, and one mol of alkali is recovered from the supernatant fluid. Compound A, therefore, must contain three atoms of sodium; this is borne out by analysis. After having dried it for more than twenty-four hours *in vacuo* at 60° C., it is found to contain 10·5% sodium, which would correspond to a compound consisting of two molecules of di-nitro-benzoic acid, one of creatinine, and three of sodium hydroxide. If Compound A is dried *in vacuo* at room temperature over calcium chloride, it contains in addition three molecules of water of crystallization.

$[(C_7H_4N_2O_2)_2$-$C_4H_7N_3O](3NaOH)$, $3H_2O$. Calculated: Na, 9·6%; N, 13·6%. Found: Na, 9·7%; N, 13·7%.

This compound, as well as all mentioned so far, does not melt. However, when heated in a capillary tube it begins to change its purple colour into a brown one at about 180° C. When exposed to air, it turns brown at room temperature within a few hours. It is easily soluble in water, less than five parts of water dissolving approximately one part of Compound A. It is only slightly soluble in ethyl alcohol. Its solubility in methyl alcohol will be discussed later. When a silver nitrate solution is added to a fresh aqueous solution of Compound A, a purple silver salt is obtained. On standing exposed to air, or on heating, this silver salt loses its purple colour and becomes a brown colour. According to analysis, this silver salt contains three atoms of silver. Therefore, the three molecules of sodium hydroxide present in Compound A have been replaced by silver.

$[(C_7H_4N_2O_2)_2\text{-}C_4H_7N_3O]3Ag$. Calculated: Ag, 37·6%. Found: Ag, 37·2%.

Compound A and Methyl Alcohol.

Compound A seems to be quite soluble in methyl alcohol and an attempt was made to use this as a means of purification. However, considerable decomposition occurs during this process, as shown by the following example.

Three grammes of Compound A are shaken vigorously with 30 c.c. of methyl alcohol. Some of the compound dissolves and the solvent takes on a deep purple colour. This solution is immediately afterwards separated rapidly from the undissolved particles by means of suction filtration through a fused glass plate. As soon as the filtration is terminated, approximately three volumes of ether are added to the filtrate. A voluminous purple precipitate is obtained, which is again separated from the supernatant fluid by filtration or centrifugation in a closed vessel; yield, 0·6 gramme. According to the sodium content of this precipitate, i.e. 10·5%, we are still dealing with Compound A. This is also supported by the analysis of the silver salt made from this precipitate. From further extracts with methyl alcohol, which on standing for about one hour turn brownish, a brown substance is precipitated on the addition of ether, which contains one molecule of creatinine, two of di-nitro-benzoic acid, four of sodium hydroxide and four of water, and which shall be called Compound B.

$[(C_7H_4N_2O_2)_2\text{-}C_4H_7N_3O]4NaOH,4H_2O$. Calculated: Na, 12·0%; N, 12·7%. Found: Na, 12·1%; N, 12·8%.

On adding silver nitrate to Compound B, a silver salt containing four molecules of silver hydroxide is obtained.

$[(C_7H_4N_2O_2)_2\text{-}C_4H_7N_3O]4AgOH$. Calculated: Ag, 41·6%. Found: Ag, 41·3%.

On extracting further with 10 c.c. lots of cold methyl alcohol, it is observed that little goes into solution and the colour of the extracted fluid is more of a reddish-brown.

However, after six extractions the extracted substance is still purple in colour ; yield, 1·4 gm. This purple substance dissolves in water with a deep red colour. On adding alcohol and ether to this solution, besides a small amount of a dark material, brownish crystals are obtained, which on qualitative tests are found to be the sodium salt of di-nitro-benzoic acid.

Compound B can also be obtained directly in a purple and " anhydrous " form from the first extract of Compound A with methyl alcohol. If this extract is concentrated at room temperature *in vacuo*, a purple powder appears which according to sodium analysis appears to be Compound B.

$[(C_7H_4N_2O_2)_2\text{-}C_4H_7N_3O]4NaOH$. Calculated : Na, 13·2% ; Found : Na, 13·4%.

Compound A and Mineral Acids.

In an attempt to isolate a purple form of creatinine di-nitro-benzoate, 7·2 c.c. N hydrochloric acid were added to 1·656 gm. of the purple form of Compound A, partly dissolved and partly suspended in 3 c.c. of water. The deep purple mixture turns towards brown on adding the acid. A brown compound is precipitated ; yield, 0·8 gm. This was recrystallized from toluol and the resulting compound up to 80 per cent. was found to be di-nitro-benzoic acid. The rest which did not dissolve in toluol is a brown substance, which has not been further investigated.

Discussion.

From the experiments described one feels justified in assuming that the purple compound or compounds underlying the reaction of creatinine with 3, 5-di-nitro-benzoic acid consist of two molecules of di-nitro-benzoic acid, one of creatinine, and most probably at least three of sodium hydroxide or of sodium respectively. The general nature of these purple compounds resembles that of the red compounds underlying Jaffe's reaction for creatinine (This Journal, 1937, *71*, 60). They are different, however, from the red compounds obtained from picric acid, inasmuch as the deep purple of all the compounds described, solid or in solution, is readily converted into a brown form. No similar marked change could be observed with the sodium containing red picric acid compounds of creatinine. The two corresponding silver salts of the di-nitro-benzoic acid compound, a purple one and a brown one, have also been obtained. This colour change from purple to brown agrees with the findings as observed in the colorimetric determination of creatinine with 3, 5-di-nitro-benzoic acid. In contrast to Jaffe's reaction, " fading ", i.e. a change of the solution from purple to brown or yellow, is more rapid with the di-nitro-benzoic acid test. Consequently this change of colour as observed in the di-nitro-benzoic acid test for creatinine must be considered, at least in its first stage, as a change from the purple form of the reaction product to the brown form. This fading with the di-nitro-benzoic acid reaction is particularly rapid in the presence of a large excess of sodium hydroxide, and in the actual test only about two molecules of sodium hydroxide are added for each molecule of sodium di-nitro-benzoate. It is therefore probable that a compound containing about three molecules of sodium hydroxide is the most likely cause of the reaction as applied analytically.

The brown form of the compounds under discussion is of considerable stability even in aqueous solution, from which it can be precipitated again in the form of its silver salt. In Compound A, for example, where this phenomenon was studied, almost complete decomposition into creatinine sodium di-nitro-benzoate and sodium hydroxide occurred after remaining in methyl alcohol for several hours. The liberated sodium hydroxide changes a small fraction of Compound A into Compound B, which differs from the original compound by an additional molecule of sodium hydroxide. The undissolved sodium-di-nitro-benzoate tenaciously retains its purple colour. This might suggest the presence of an isomeric purple form of sodium-di-nitro-benzoate, the existence of which seems quite probable in view of the fact that a purple colour of a fleeting nature is obtained when di-nitro-benzoic acid is dissolved in an excess of sodium hydroxide. However, at this stage no attempt will be made to elucidate the nature of the coloration of any of the compounds mentioned in this paper. This will be done in conjunction with other similar compounds. The formulæ in the text are put forward tentatively, and will be under revision on that occasion.

SUMMARY.

If the reaction for creatinine with 3, 5-di-nitro-benzoic acid and sodium hydroxide is performed in an alcoholic medium, crystalline compounds of a deep purple colour

are readily obtained. They consist of two molecules of di-nitro-benzoic acid, one of creatinine, and varying amounts of sodium hydroxide or sodium, depending to a large extent on the amount of sodium hydroxide added. They exist in two forms, a purple and a brown one, the latter being more stable. One of these compounds, containing three molecules of sodium hydroxide, decomposes in methyl alcohol into sodium di-nitro-benzoate, creatinine and a creatinine di-nitro-benzoate, containing four molecules of sodium hydroxide.

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THE VISCOSITIES OF SOME COMPLEX SALTS IN AQUEOUS SOLUTION.

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If one compares the viscosities of substances either alone or in solution, one would expect to find that those substances which had the larger molecules would also have the greater viscosities. This is, however, not always the case. For example the viscosity of cæsium ion in aqueous solution is less than that of the sodium ion.⁽¹⁾ The Cr_2O_7'' ion has a smaller viscosity than the CrO_4'' ion.⁽²⁾ Blanchard⁽³⁾ showed that a solution of tetrammine cupric sulphate has a lower viscosity than a solution of cupric sulphate.

We thought that it would be of interest to determine the viscosity of aqueous solutions of other complex salts.

Instead of preparing separately in every case the complex salt to be experimented on, we have added certain substances to pure (simple) salts in solution, thereby forming to a greater or less extent complex salts in solution. We have found that solutions of the compounds formed between ethylenediamine and copper salts (chloride, sulphate, nitrate) have a lower viscosity than the corresponding solutions of the simple salts. Solutions of the compounds of zinc and nickel sulphates with ethylenediamine have a scarcely greater viscosity than those of the simple salts, while solutions of the compounds of silver nitrate and cobalt chloride with ethylenediamine show decidedly greater viscosity than those of the simple salts. Solutions containing pyridine and salts of nickel, cobalt, zinc and silver have all got a definitely greater viscosity than the solutions of the simple salts.

The low values obtained for the viscosities of the solutions of complex salts containing ethylenediamine would lead us to expect higher values for the conductivities of these salts. Experiments carried out on the conductivities of zinc salts and of copper salts to which ethylenediamine has been added show that these complex salts have, in dilute solutions, somewhat greater values for electrical conductivity than the simple salts.

We suggest that the very considerable number of water molecules surrounding each Cu^{++} ion in a simple cupric salt is displaced by a much smaller number of ethylenediamine molecules giving an ion of not less mobility than the original one. At the same time a considerable number of free water molecules is liberated. The proportion of solute molecules to solvent molecules is thus lowered.

SYSTEMATIC PART.

In this paper the viscosity of dilute solutions is considered. By a dilute solution is here meant a solution in which the concentration is usually not greater than molecular (one gram-mol. per litre). In this paper the " relative viscosity" (water=1) is also used throughout in preference to " absolute viscosity ".

A great deal of discussion⁽⁴⁾ has taken place among workers on the viscosity of solutions as to the best way to express the relation between the viscosity of a solution and its concentration. The older Arrhenius formula is $\eta = A^x$, or $\eta = 1 + x \log_e A + \frac{x^2 \log^2_e A}{2} + \ldots$ where " η " is the (relative) viscosity at any fixed temperature, " A " is a constant, and " x " is the concentration of the solute. This formula is usually reducible for dilute solutions to

$$\eta = 1 + ax$$

where $a = \log_e A$.

Many other formulæ⁽⁴⁾ have been suggested. Instead of $1 + ax$ or $1 + ax + bx^2$ etc....., formulæ in which the square root of the concentration appears have been proposed. Jones and Dole use an expression $\eta + 1 + A\sqrt{x} + (A - B)x$⁽⁵⁾ while Falkenhagen⁽⁶⁾ uses the formula $\eta = 1 + A\sqrt{x}$. Nevertheless, for dilute solutions of both electrolytes and non-electrolytes the linear function $\eta = 1 + ax$, or the Arrhenius formula $\eta = A^x$ are quite suitable for the purpose of this work.

The Arrhenius exponential formula (see Euler, *Zeit. für physikal. Chemie*, 1898, *25*, 536) suggests that the viscosity of a solution containing two salts in the same solution is given by the product of the (relative) viscosities of the two separate solutions.

Thus $\eta_A = A^x$ and $\eta_B = B^y$ give $\eta_{A+B} = A^x B^y$ .... (I)

Using the linear formula

$$\eta_A = 1 + ax$$
$$\eta_B = 1 + by$$
$$\eta_{A+B} = (1 + ax)(1 + by)$$
$$= 1 + ax + by + axby \quad \text{.................} \quad \text{(II)}$$

For smaller concentrations (x and y small), this becomes

$$1 + ax + by \quad \text{.........................} \quad \text{(III)}$$

The conclusions drawn in the present research from the viscosities of solutions containing more than one solute are those from numbers involving the product of viscosities (equation II above), but no great change in the conclusions would have to be made if, instead, equation III had been used.

The Ostwald viscosimeter was used for the determination of viscosity in the work.

Viscosity of a Solution Containing Several Solutes.

(i) When there is no combination between solute and solvent, or between solute and another solute, it is assumed that the (relative) viscosity of a solution containing two solutes is equal to the product of the (relative) viscosities of two separate solutions each containing one of the solutes only.

The following numbers obtained by us show the agreement between observed and calculated values.

Table I.

Solute.	(Relative) Viscosity of each Solute at 25° C.	Product of the Two Viscosities.	Observed Value for Solution containing Two Solutes.
0·5 N KCl	0·995	1·040	1·043
1·0 N Urea	1·045		
0·818 M NH_4OH ..	1·032	1·164	1·170
0·5 M $BaCl_2$	1·129		
0·63 M Ethylene-diamine	1·064	1·137	1·136
0·25 M $BaCl_2$ ..	1·069		

(ii) When there is combination between the solutes, one would expect a divergence between the calculated and observed values.

The following results were obtained with aqueous solutions :

TABLE II.

Solute.	Relative Viscosity of each (Separate) Solute (25° C.).	Product.	Observed Value.
0·5 N HCl	1·033	1·146	1·045
0·5 N NaOH ..	1·109		
0·5 HCl	1·033	1·184	1·078
0·5 N $N(CH_3)_4OH$ ..	1·146		

Dividing the calculated value by the observed value gives 1·097 and 1·099 respectively.

The divergence between calculated and observed value may be taken as due in both cases to the same cause—the formation of water from the H^+ and OH^- ions.

(iii) Combination between the solutes will not usually result, as in Table II, in the formation of more solvent. A new solute or solutes will be formed. These new solute molecules will have a different size and shape from the original solute molecules. Further, the sheath of solvent molecules attached to the solute molecule will alter the magnitude⁽⁶⁾ of the solute molecules.

Interesting results were obtained by Blanchard⁽⁷⁾ on aqueous solutions of the complex salts obtained by addition of ammonia to solutions of copper (and silver) salts. A solution of the cuprammonium salts gave a smaller viscosity than that of the original copper salt. Joyner⁽⁸⁾ later found that in the case of cuprammonium cellulose solutions the viscosity decreases very considerably with even larger amounts of ammonia than correspond to the usual cuprammine salt. Some further experiments have been carried out by us in continuance of this rather remarkable phenomenon observed first by Blanchard.

In the following table (III) results are given for the effect on the viscosity of solutions of copper salts by addition of some substance other than ammonia. In all these (four) cases the observed is less than the calculated viscosity.

Table III.

	Viscosity (25° C.).	Product.	Observed Viscosity.
0·25 M $Cu(NO_3)_2$ ..	1·119	1·223	1·102
0·75 M En* ..	1·093		
0·25 M $Cu(NO_3)_2$ ..	1·119	1·135	1·120
0·25 M Urea ..	1·014		
0·25 M $Cu(NO_3)_2$ ..	1·119	1·555	1·394
0·25 M Sucrose ..	1·39		
0·29 M $[Cu\text{-}En_2](NO_3)_2$	1·102	1·532	1·403
0·25 M Sucrose ..	1·39		

*En = Ethylenediamine.

Diminution in viscosity when complex salts are formed is not a general one, as can be seen from the results of the following experiments.

Table IV.

	Viscosity.	Product.	Observed Viscosity.
0·4 M KNO_3 ..	0·991	1·0	1·013
0·2 M $AgNO_3$ ..	1·009		
0·2 M $AgNO_3$ ..	1·009	0·998	1·019
0·8 M KCN	0·990		

While there is a negligible amount of complex salt formed when potassium nitrate and silver nitrate are mixed, a complex salt is definitely formed when excess of potassium cyanide and silver nitrate are mixed. Although the complex salt $KAg(CN)_2$ is formed, it will be seen that no diminution in the observed viscosity due to its formation can be detected here.

The alteration in the viscosity of metallic salts shown after the addition of ethylenediamine was next investigated more particularly, the compounds formed being more stable in solution than the corresponding ammonia compounds.

In the following tables are given the viscosity of ethylenediamine solutions and of various salt solutions to which ethylenediamine was added.

Table V.

Ethylenediamine in aqueous solution (25° C.).

Concentration.	Viscosity.
0·2 N (0·1 molec.)	1·021
0·4 N	1·042
0·8 N	1·085
1·3 N	1·140
1·6 N	1·179
3·2 N	1·418

Table VI.

0·1 N (=0·05 mol.) cupric chloride with additions of ethylenediamine.

Concentration of Ethylenediamine.	Viscosity Calculated.	Viscosity Observed.
0	—	1·023
0·2 N (=0·1 molec.)	1·044	1·021
0·4 N	1·064	1·021
1·0 N	1·132	1·050

Table VII.

0·2 N $CuCl_2$ with additions of ethylenediamine.

Concentration of Ethylenediamine.	Viscosity Calculated.	Viscosity Observed.
0	—	1·043
0·4 N	1·087	1·033
0·8 N	1·131	1·047
1·6 N	1·230	1·084

Table VIII.

N (=0·5 molec.) $CuCl_2$ with additions of ethylenediamine.

Concentration of Ethylenediamine.	Viscosity Calculated.	Viscosity Observed.
0	—	1·217
2·6 N	1·60	1·16
4·45 N	2·009	1·21
8·9 N	—	1·56

Table IX.

0·2 N (=0·1 molec.) $CuSO_4$ with additions of ethylenediamine.

Concentration of Ethylenediamine.	Calculated Viscosity.	Observed Viscosity.
0	—	1·090
0·32 N	1·126	1·069
0·4 N	1·135	1·074
0·8 N	1·183	1·106

Table X.

0·5 molar silver nitrate with additions of ethylenediamine.

Concentration of Ethylenediamine.	Calculated Viscosity.	Observed Viscosity.
0	—	1·020
0·64 N	1·084	1·059
0·78 N	1·100	1·068
0·914 N	1·116	1·089
1·250 N	1·157	1·131

Table XI.

0·2 N (=0·1 molec.) zinc sulphate with addition of ethylenediamine.

Concentration of Ethylenediamine.	Calculated Viscosity.	Observed Viscosity.
0	—	1·067
0·464 N	1·117	1·071
0·514 N	1·122	1·073
0·59 N	1·130	1·077
0·628 N	1·133	1·083
0·81 N	1·154	1·099
1·25 N	1·210	1·139

TABLE XII.

0·2 N (=0·1 molec.) nickelous sulphate with additions of ethylenediamine.

Concentration of Ethylenediamine.	Calculated Viscosity.	Observed Viscosity.
0	—	1·069
0·142 N	1·086	1·068
0·186 N	1·089	1·065
0·274 N	1·099	1·072
0·428 N	1·115	1·079
0·560 N	1·129	1·086
1·244 N	1·212	1·168

TABLE XIII.

0·2 N (=0·1 molec.) cobaltous sulphate with additions of ethylenediamine.

Concentration of Ethylenediamine.	Calculated Viscosity.	Observed Viscosity.
0	—	1·040
0·748 N	1·117	1·071
1·48 N	1·208	1·156
2·20 N	1·298	1·257

In all cases (Tables VI-XIII) the observed viscosity is considerably less than the calculated viscosity. In the case of the copper salts the complex salt has always a lower viscosity than the original simple salt. In the case of nickel and zinc sulphates the viscosities of the complex salts are about the same as those of the simple salts. In the case of cobalt sulphate the complex salt has a greater viscosity than that of the simple salt.

The viscosities of some pyridine solutions are next given.

TABLE XIV.

Pyridine solutions (in water), 25° C.

Concentration.	Viscosity.
0·703 mol.	1·152
1·380	1·313
2·097	1·482
2·720	1·655

TABLE XV.

0·1 molec. silver nitrate with additions of pyridine.

Concentration of pyridine.	Calculated Viscosity.	Observed Viscosity.
0	—	1·010
0·334	1·083	1·093
0·693	1·161	1·174
1·027	1·241	1·260

TABLE XVI.

0·1 mol. nickel sulphate with additions of pyridine.

Concentration of pyridine.	Calculated Viscosity.	Observed Viscosity.
0	—	1·069
0·260 mol.	1·129	1·141
0·680	1·226	1·251
0·990	1·304	1·349

The mixtures of pyridine with zinc sulphate and cobaltous chloride produced precipitates.

It will be seen that the observed viscosities are here greater than the calculated viscosities. The complex salts with pyridine have evidently greater viscosity than the simple salts. This indeed might be expected from the larger molecules involved.

INVESTIGATION OF OTHER PROPERTIES.

The lowered viscosities obtained when ethylenediamine is added to copper salts suggested to us that we might examine some other properties of these solutions.

In the first place it was thought advisable to test whether there was any abnormal volume change when copper ethylenediamine nitrate is mixed with water. The solid was found to have a density of 1·677 at 25° C., while the 0·293 M solution (containing 101·0 grammes of the solid, $CuEn_2(NO_3)_22H_2O$, in a litre of solution) had a density of 1·044. This shows that a contraction of 6·7 c.c. occurs in making up one litre of 0·293 M solution. In making up a

0·293 molecular solution of copper sulphate a contraction of 3 c.c. occurs. The contraction when the complex salt is dissolved is therefore not to be considered abnormal when we remember that the contraction on dissolving sodium hydroxide in water is of about the same magnitude as the volume of the hydroxide dissolved. There is evidently no abnormal contraction on solution of these complex salts of copper to correspond to the abnormally low viscosities.

It is not so very remarkable that the viscosity of $[CuEn_2]^{++}$ or $[CuEn_3]^{++}$ is less than the (combined) viscosities of Cu^{++} and 2 En or 3 En, for there are fewer solute molecules due to the combination. But that $[CuEn_2]^{++}$ should have a smaller viscosity than Cu^{++} is indeed rather extraordinary.

Now, if the viscosity of $Cu(NH_3)_4^{++}$ or $[CuEn_2]^{++}$ is less than that of Cu^{++} one would expect that the electrical conductivity of the complex copper salts in solution would be greater than the conductivity of the corresponding (simple) copper salts. Reychler⁽⁹⁾ showed that the ion $Cu(NH_3)_4^{++}$ has a mobility not noticeably different from that of Cu^{++}.

The electrical conductivity of copper ethylenediamine nitrate in water was kindly determined for the authors by Dr. T. Iredale, with the following results :

Concentration.	Molecular Conductivity (25° C.).
0·058 mol. (=0·116 N)	85·5
0·0145 mol.	107·0
0·0036 mol.	121·5
0·00045 mol.	130·5

The values for copper nitrate are as follows :

0·05 mol.	94·0
0·025 mol.	101·0
0·01 mol.	108·0
0·005 mol.	114·0
0·0025 mol.	117·0

The results indicate that the complex salt in very dilute solution has a slightly greater electrical conductivity than the simple copper nitrate.

We have also determined the electrical conductivity of zinc sulphate solutions and of ethylenediamine zinc sulphate solutions. The zinc sulphate ($ZnSO_47H_2O$) was purified by recrystallization and the complex salt prepared by mixing ethylenediamine and zinc sulphate solutions. The salt obtained was found by analysis to correspond exactly to $ZnEn_3(SO_4)$.

The following results were obtained :

Zinc Sulphate $\frac{1}{2}\{ZnSo_47H_2O\}$.

Concentration.	Dilution in Litres.	Specific Conductivity (25° C.).	Equivalent Conductivity.
N/10 (=M/20)	10	$5 \cdot 293 \times 10^{-3}$	52·9
N/50	50	$1 \cdot 495 \times 10^{-3}$	74·7
N/500	500	$2 \cdot 225 \times 10^{-4}$	111·2
N/5000	5,000	$2 \cdot 81 \times 10^{-5}$	140·4

Ethylenediamine Zinc Sulphate $\frac{1}{2}\{ZnEn_3(So_4)\}$.

Concentration.	Dilution in Litres.	Specific Conductivity (25° C.).	Equivalent Conductivity.
N/10 (=M/20)	10	$6 \cdot 683 \times 10^{-3}$	66·8
N/50	50	$1 \cdot 734 \times 10^{-3}$	86·7
N/500	500	$2 \cdot 425 \times 10^{-4}$	121·2
N/5000	5,000	$3 \cdot 187 \times 10^{-5}$	159·8

The results indicate that the complex zinc salt has a somewhat greater conductivity than the simple salt.

Although at first it seems rather remarkable that the ions $[CuEn_2]^{++}$ and $[ZnEn_3]^{++}$ should have lower viscosity and a greater mobility than the simple ions Cu^{++} and Zn^{++}, it is possible that this can be accounted for by assuming that there are a rather large number of water molecules attached to the Cu^{++} and Zn^{++} ions. The exact number of water molecules as determined by different methods varies a good deal. According to Brintzinger, Ratanarat and Osswald⁽¹⁰⁾ the number attached to Cu^{++} is 38 (0·1 N concentration). Another determination by Brintzinger and Ratanarat⁽¹¹⁾ gives the copper number as 24. Riesenfeld and Remhold⁽¹²⁾ give the number as 56 for $\frac{1}{2}$ Cu^{++}. Remy⁽¹³⁾ gives the number 48 for $\frac{1}{2}$ Cu^{++} in dilute solutions. It seems fairly certain that the number is at least 16. Now when ethylenediamine is added to the solutions, either 2 or 3 molecules adhere to the copper ion and probably displace these 16 or more water molecules. This may give a smaller ion than the one with the water molecules attached. Besides this, a relatively large number of water molecules are added to the solvent thus making a more dilute solution than the calculated value.

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R—October 6, 1937.

HETEROCYCLIC COMPOUNDS DERIVED FROM CATECHOL ETHERS.

Part I. Some Derivatives of 6 : 7-Dimethoxy Quinoline.

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(*Manuscript received, September 22, 1937. Read, October 6, 1937.*)

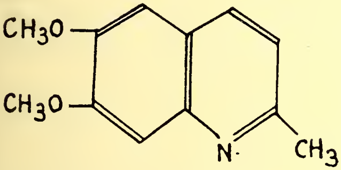
In a discussion of the question of the entry of substituents into the catechol nucleus, Jones and Robinson (*J.C.S.*, 1917, 903) pointed out that:

"(*a*) In the preparation of mono-substituted catechol ethers only the 4-derivative is obtained.

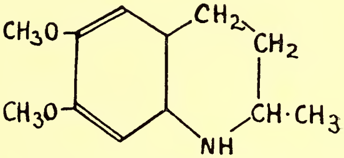
"(*b*) Disubstituted catechol ethers are 4 : 5-derivatives."

These generalisations have been amply borne out by experience, the single well authenticated exceptional reaction being the bromination of nitroveratrole, but up to the present the possibility of utilising this marked concentration of reactivity of catechol ethers on the 4 and 5 carbon atoms in order to attach fused heterocyclic rings of various types containing these adjacent carbon atoms 4 and 5 as common ring members, has been systematically explored for only a few heterocyclic systems. The catechol nucleus occurs so frequently in compounds elaborated naturally, and substances containing it are often of such vital biochemical significance—cf. adrenaline—that all work on derivatives of catechol may be deemed of importance. Among the heterocyclic types of outstanding importance containing the catechol nucleus, by far the most important is that of the iso-quinolines, almost all of the important isoquinoline alkaloids containing catechol ether nuclei. Moreover, it is becoming increasingly apparent that some important naturally occurring substances (e.g. brucine and melanin) are derived from 5 : 6-dihydroxyindole; so that systematic exploration of indole derivatives containing catechol nuclei is indicated. The oxygen heterocyclics with catechol nuclei have, also, not been neglected by nature, and recent work—on rotenone, and on brazilin, hæmatoxylin and other plant pigments—has indicated their importance. The author has consequently decided to commence a systematic investigation of synthetic heterocyclic substances containing catechol ether nuclei, and particularly to study some of the types which so far have been relatively neglected.

In the present paper are described certain new derivatives of 6 : 7-dimethoxy quinoline which are comparatievly easy to prepare pure in good yield. Thus, application of the Döbner-Miller reaction to 4-aminoveratrole—condensation with paraldehyde in presence of concentrated hydrochloric acid containing zinc chloride—gives good yields of 6 : 7-dimethoxyquinoline (I), a white crystalline substance melting at 103°, previously prepared by Rilliet (*Helv. Chim. Acta*, 1922, *5*, 547-552) by condensing 6-aminoveratric aldehyde with acetone.



I.

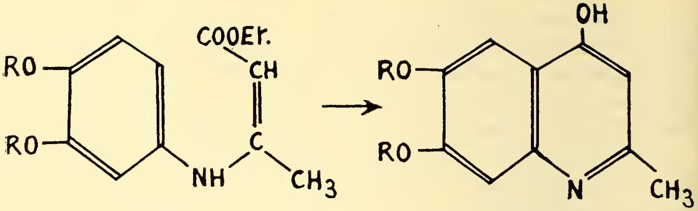


II.

Reduction of (I) with sodium and absolute ethyl alcohol gives 2-methyl-6 : 7-dimethoxy-1 : 2 : 3 : 4-tetrahydroquinoline (II), the acetyl derivative of which shows the brucine reaction with nitric acid (cf. Lions, Perkin, and Robinson, *J.C.S.*, 1925, 1158). 6 : 7-Dimethoxyquinoline (I) readily forms a crystalline methiodide and a crystalline ethiodide.

4-Aminoveratrole reacts rapidly with ethyl acetoacetate in the cold in presence of a trace of hydrochloric acid (cf. Coffey, Thomson, and Wilson, *J.C.S.*, 1936, 856) with elimination of water and formation of ethyl β-(3 : 4-dimethoxy-anilino)-crotonate (III ; $R = CH_3$), a practically colourless crystalline solid, which is rapidly cyclised to 2-methyl-4-hydroxy-6 : 7-dimethoxy quinoline (IV ; $R = CH_3$) by dropping it into paraffin oil previously heated to 270° (cf. Limpach, *Berichte*, 1931, *64*B, 969-70).

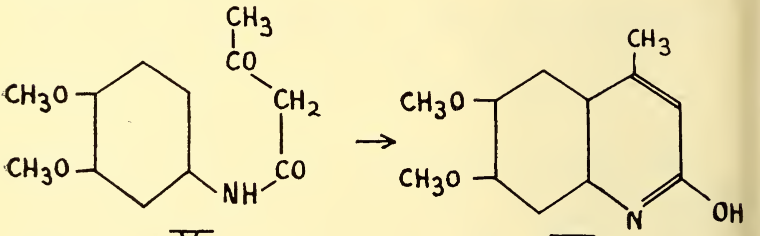
In a similar way 4-aminocatechol diethyl ether can be condensed with ethyl acetoacetate to ethyl β-(3′ : 4′-diethoxyanilino)-crotonate (III ; $R = C_2H_5$), an oil which could not be induced to crystallise, but which cyclises



III. IV.

readily in hot paraffin oil to the crystalline 2-methyl-4-hydroxy-6 : 7-diethoxy quinoline (IV ; R $=C_2H_5$).

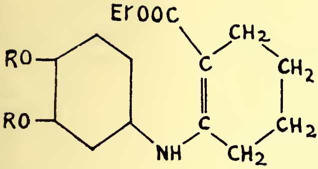
Solution of 4-aminoveratrole in four times its weight of ethyl acetoacetate previously heated to 160°, and maintenance of this temperature for 5 minutes, followed by cooling and then removal of the excess ester *in vacuo* leads to formation of 4-acetoacetamidoveratrole (V), a white crystalline solid, readily transformed by concentrated sulphuric acid to 2-hydroxy-4-methyl-6 : 7-dimethoxy quinoline (VI).



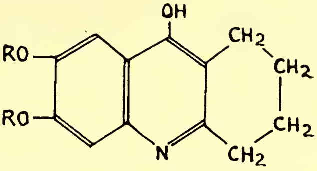
V. VI.

4-Aminoveratrole condenses rapidly even in the cold with ethyl cyclohexanone-2-carboxylate in presence of a trace of hydrochloric acid, giving ethyl-2-(3′ : 4′-dimethoxyanilino)-Δ^1-cyclohexene-1-carboxylate (VII ; R $=CH_3$), and solution of this crystalline solid in eight times its weight of paraffin oil previously heated to 280° leads to rapid cyclisation and formation of 5-hydroxy-7 : 8-dimethoxy-1 : 2 : 3 : 4-tetrahydro acridine (VIII ; R $=CH_3$), a well crystallised, insoluble, high melting solid.

4-Aminocatechol diethyl ether also condenses readily with ethyl cyclohexanone-2-carboxylate to the low melting ester (VII ; R $=C_2H_5$) and this is readily cyclised by solution in hot paraffin oil to 5-hydroxy-7 : 8-diethoxy-1 : 2 : 3 : 4-tetrahydroacridine (VIII ; R $=C_2H_5$), a solid of high melting point.

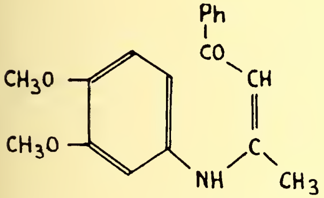


VII.

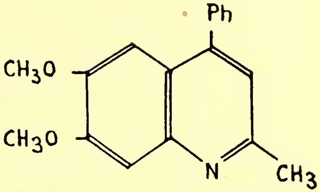


VIII.

Finally, 4-aminoveratrole condenses readily with benzoylacetone to a Schiff's base which is almost certainly β-(3′ : 4′-dimethoxyanilino)-propenyl phenyl ketone (IX) (cf. Beyer, *Berichte*, 1887, *20*, 1767 ; Geigy and Koenigs, *Ibid.*, 1885, *18*, 2406). Solution of (IX) in concentrated sulphuric acid effects quinoline ring closure, with formation of 2-methyl-4-phenyl-6 : 7-dimethoxyquinoline (X).



IX.



X.

Attempts to prepare 2-phenyl-4-methyl-6 : 7-dimethoxy quinoline by condensation of 6-aminoacetoveratrone with acetophenone in aqueous alcoholic or alcoholic alkaline solution all proved abortive.

EXPERIMENTAL.

2-Methyl-6 : 7-dimethoxy quinoline (*I*).

4-Aminoveratrole (Fargher, *J.C.S.*, 1920, 869) (15·3 grams) was dissolved in concentrated hydrochloric acid (35 c.c.) with warming, and after addition of anhydrous zinc chloride (5 g. ; cf. Mills, Harris, and Lambourne, *J.C.S.*, 1921, 1294) the solution was cooled to 20°, when a mass of bluish crystals was deposited. Paraldehyde (20 g.) was then added in one lot, and the mixture vigorously shaken. The crystals gradually went into solution, the colour changed to green and the temperature fell. Small light green granules then commenced to deposit and the mixture became quite pasty. It was gently warmed to about 30° and allowed to stand. After a short time the separated solid went into solution, the liquid became brown in colour, and heat was evolved. A few minutes after this a mass of almost colourless crystals separated. Further heating produced no apparent change. The reaction mixture was treated with a large excess of sodium hydroxide solution, the liberated bases separated by means of ether, then dissolved in dilute acid and treated with nitrous acid to remove secondary bases. After recovery from the acid solution the tertiary base was taken up, washed and dried in ether, and after removal of the solvent, distilled *in vacuo.* A thick, yellow, oily liquid (8 g.) boiling at 195-200°/4 mm. was collected. Allowed to stand, it soon crystallised, and after recrystallisation from light petroleum ether was obtained in minute white prisms melting at 103°. Rilliet (*loc. cit.*) gives the same melting point.

Found: C=70·7, H=6·5, N=7·2%; calculated for $C_{12}H_{13}O_2N$, C=70·9, H=6·4, N=6·9%.

The base is very soluble in alcoholic solvents, and such solutions immediately deposit a voluminous precipitate of the *picrate* when treated with alcoholic picric acid. In agreement with Rilliet (*loc. cit.*) it melts at 217°. It is a very insoluble substance.

Found: N=13·4%; calculated for $C_{18}H_{16}O_8N_4$, N=13·5%.

Solution of the base (I) in excess of methyl iodide with gentle warming leads to very rapid production of the *methiodide*, which is precipitated almost immediately. Recrystallised from much boiling alcohol, it is obtained in practically colourless prisms melting at 241°.

Found: N=4·2%; calculated for $C_{13}H_{16}O_2NI$, N=4·1%.

The *ethiodide* of (I) is also readily obtained by heating a solution of (I) in excess ethyl iodide under gentle reflux for 30 minutes. Recrystallised from much ethyl alcohol it is obtained in colourless prisms.

Found: N=3·8%; calculated for $C_{14}H_{18}O_2NI$, N=3·9%.

Ethyl-β-(3 : 4-dimethoxyanilino)-crotonate (III ; R=CH$_3$).

4-Aminoveratrole (15·3 g.) and acetoacetic ester (13·0 g.) were warmed together on the water-bath until a homogeneous liquid was obtained. After cooling to room temperature one drop of 5N hydrochloric acid was added to the cooled liquid. Water commenced to separate immediately. After standing overnight the oil was taken up and dried in ether, and after removal of the solvent and cooling it crystallised. It was best recrystallised from light petroleum in which it is moderately soluble. In most of the other organic solvents, particularly the lower alcohols, it is very soluble. Almost colourless prisms, m.p. 61°. The yield was practically quantitative.

Found : N=5·5% ; calculated for $C_{14}H_{19}O_4N$, N=5·3%.

2-Methyl-4-hydroxy-6 : 7-dimethoxy quinoline (*IV ; R*=CH_3)

The substituted anilino crotonic ester (III) (10 g.) was melted and added in one lot to high boiling paraffin oil (60 g.) pre-heated to 270°. A vigorous ebullition occurred and after about a minute the quinoline derivative commenced to separate. The solution was maintained at 260° for five minutes, then cooled. The separated brownish solid was freed from paraffin by filtration and washing with petroleum ether followed by ordinary ether. It was then boiled with a little alcohol, when the substances responsible for the brown colour went into solution, leaving hard crystalline nodules, which were eventually recrystallised from much alcohol and thus obtained in minute prisms, m.p. 280°. Yield, 70%.

Found : N=6·7% ; calculated for $C_{12}H_{13}O_3N$, N=6·4%.

2-Methyl-4-hydroxy-6 : 7-diethoxy quinoline (*IV ; R*=C_2H_5).

3 : 4-Diethoxyaniline (9 g.) and ethyl acetoacetate (6·5 g.) were gently warmed together until a homogeneous solution was obtained. After cooling to room temperature one small drop of 5N hydrochloric acid was added. Water commenced to separate almost immediately. The mixture was allowed to stand overnight, the oil was taken up, washed, and dried in ether. After removal of the solvent a brownish oil—ethyl β-(3′ : 4′-diethoxyanilino)-crotonate—remained. It could not be induced to crystallise, so was warmed to 100° and then dropped into five times its weight of paraffin oil previously heated to 280°. A vigorous reaction occurred and the quinoline derivative soon commenced to separate as an oil. It solidified on cooling and was recovered from the paraffin by filtration and washing with petroleum ether. Eventually it was purified by recrystallisation from alcohol and thus

obtained in minute very pale yellow prisms, m.p. 211°. Yield, 50%.

Found: C=67·2, H=6·7%; calculated for $C_{14}H_{17}O_3N$, C=68·0, H=6·9%.

4-Acetoacetamidoveratrole (*V*).

4-Aminoveratrole (5 g.) was melted and added in one lot to acetoacetic ester (20 g.) previously rapidly heated to 160°. The liquid boiled, ethyl alcohol being probably boiled off. The mixture was maintained at 160° for five minutes, was then partially cooled and the excess acetoacetic ester distilled off *in vacuo*. The reddish brown residue slowly crystallised. After pressing on a porous tile, the crystalline material was recrystallised from petroleum ether. Perfectly white minute prisms (yield 60%) melting at 59° were thus obtained.

Found: N=6·0%; calculated for $C_{12}H_{15}O_4N$, N=5·9%.

2-Hydroxy-4-methyl-6:7-dimethoxyquinoline (*VI*).

The anilide (V) was dissolved in four times its weight of ice-cold concentrated sulphuric acid and after 15 minutes in the cold was allowed to warm to room temperature. After standing two hours it was poured into cold water and the solution at once basified with ammonia. A pale pink flocculent precipitate separated, which was collected, washed with water and recrystallised from methyl alcohol. It was thus obtained in small, colourless, crystalline granules, m.p. 235°.

Found: N=6·4%; calculated for $C_{12}H_{13}O_3N$, N=6·4%.

Ethyl-2-(3′:4′-dimethoxyanilino)-$\triangle'$-cyclohexene-1-carboxylate (*VII*; *R*=*CH_3*).

4-Aminoveratrole (15·3 g.) was carefully dissolved with gentle warming in ethyl cyclohexanone-2-carboxylate (17·0 g.). After cooling and addition of one drop of 5N hydrochloric acid water commenced to separate almost immediately. Reaction was complete within an hour. The oily reaction mixture solidified on standing overnight, and the solid was recrystallised from methyl alcohol and thus obtained in minute, almost colourless prisms, m.p. 72°. Yield, 90-95%.

Found: N=4·9%; calculated for $C_{17}H_{23}O_4N$, N=4·6%.

5 - Hydroxy - 7 : 8 - dimethoxy - 1 : 2 : 3 : 4 - tetrahydroacridine (VIII; $R=CH_3$).

Solution of the Schiff's base (VII, $R=CH_3$; 16 g.) in high boiling paraffin oil (100 g.) at 270° led to an immediate reaction, alcohol being evolved, a yellow colour developing at once, and a cream-coloured solid separating almost immediately. The reaction mixture was kept at 260° for five minutes and was then cooled. The separated cream precipitate was freed from paraffin by filtration and thorough washing with petroleum ether. It was very sparingly soluble in the usual organic solvents except glacial acetic acid. When recrystallised from a hot solvent such as hot ethyl alcohol it came out only very slowly on standing, in minute prisms, melting above 300°. The yield was over 80%.

Found : N=5·5% ; calculated for $C_{15}H_{17}O_3N$, N=5·7%.

The base (VIII; $R=CH_3$) dissolves fairly readily in hot alcohol containing some concentrated hydrochloric acid and on cooling fine white needles of the *hydrochloride* melting at 244° separated.

Found : N=4·7% ; calculated for $C_{15}H_{18}O_3NCl$, N=4·7%.

Ethyl - 2 - (3′ : 4′ - diethoxyanilino) - $\triangle'$ - cyclohexene - 1 - carboxylate (VII; $R=C_2H_5$).

3 : 4-Diethoxyaniline (9 g.) was condensed with ethyl cyclohexanone-2-carboxylate (8·5 g.) in the cold in presence of a drop of hydrochloric acid exactly as described for the dimethoxy compound. The yield was practically quantitative. The product was a low melting solid very difficult to recrystallise, owing to its solubility, but eventually it was recrystallised from petroleum ether and obtained in small colourless prisms, m.p. 44°.

Found : N=4·4% ; calculated for $C_{19}H_{27}O_4N$, N=4·2%.

5 - Hydroxy - 7 : 8 - diethoxy - 1 : 2 : 3 : 4 - tetrahydroacridine (VIII; $R=C_2H_5$).

The above-described Schiff's base (VII; $R=C_2H_5$) was dissolved in six times its weight of paraffin oil previously heated to 280°. Reaction was immediate, alcohol was evolved and the acridine commenced to separate almost at once. It was recovered from the cooled paraffin and eventually recrystallised from much alcohol, being obtained in minute pale yellow prisms, m.p. 281°. Yield, 70%.

Found: N = 3·7%; calculated for $C_{17}H_{21}O_3N$, N = 3·6%.

β-(*3 : 4-Dimethoxyanilino*)-*propenyl-phenyl-ketone* (*IX*).

4-Aminoveratrole (5·1 g.) and benzoylacetone (5·4 g.) were melted together to a homogeneous liquid on a boiling water-bath. One small drop of 5N hydrochloric acid was then added. Water commenced to separate within a few minutes and the reaction was complete within an hour. On cooling and allowing to stand the oil crystallised. After two recrystallisations from hot ethyl alcohol the substance was obtained in very faintly yellow prisms, m.p. 100°. The yield was practically quantitative.

Found: N = 5·0%; calculated for $C_{16}H_{19}O_3N$, N = 4·7%.

2-Methyl-4-phenyl-6 : 7-dimethoxy quinoline (*X*).

The above-described Schiff's base (IX; 6 g.) was dissolved gradually in cold concentrated sulphuric acid (20 c.c.). The solid became intense yellow on contact with the sulphuric acid and then went into solution with evolution of heat and fading of the colour to a pale yellow, and development of a blue fluorescence. After standing overnight out of contact with air the solution was poured into water and the solution basified with excess sodium hydroxide solution. A very pale yellow oil separated, and this was induced to crystallise. After collection on a filter and washing with water it was recrystallised from methyl alcohol. It was apparently a hydrate, for it was low melting. However, contact with the methyl alcohol seemed to dehydrate it and the product which separated from this solvent formed hard granular prisms, melting at 142°. Yield, 80-90%.

Found: N = 5·2%; calculated for $C_{18}H_{17}O_2N$, N = 5·0%.

ACKNOWLEDGMENT.

The author desires to express his grateful thanks to Miss E. M. Goulston, B.Sc., for several of the analyses recorded in this paper.

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HETEROCYCLIC COMPOUNDS DERIVED FROM CATECHOL ETHERS.

PART II. SOME 7 : 8-DIMETHOXYQUINOLINES AND SOME 5 : 6 : 7-TRIMETHOXYQUINOLINES.

By JOHN NEVIL GRAVES,
GORDON K. HUGHES, B.Sc.,
and FRANCIS LIONS, B.Sc., Ph.D.

(*Manuscript received, September 22, 1937. Read, October 6, 1937.*)

In the present paper are described the preparation of the 4-hydroxyquinaldines and the 2-hydroxylepidines from 3-aminoveratrole (I) and 5-aminopyrogallol trimethyl ether (II). Condensation of these bases (I and II) with ethyl acetoacetate in the cold in presence of a small amount of hydrochloric acid yields the corresponding β-anilinocrotonic esters, which can be readily cyclised to 2-methyl-4-hydroxy-7 : 8-dimethoxyquinoline (III) and 2-methyl-4-hydroxy-5 : 6 : 7-trimethoxyquinoline (IV) respectively by dropping them into paraffin oil previously heated to 280°. (Cf. Limpach, *Berichte*, 1931, *64*B, 969-70.)

Condensation of the bases (I) and (II) with ethyl acetoacetate at 140° leads to formation of the corresponding acetoacetanilides and these can be cyclised by solution in concentrated sulphuric acid to 2-hydroxy-4-methyl-7 : 8-dimethoxyquinoline (V) and 2-hydroxy-4-methyl-5 : 6 : 7-trimethoxyquinoline (VI) respectively.

Further, the bases (I) and (II) can be condensed with ethyl cyclohexanone-2-carboxylate to form the corresponding cyclohexene carboxylic esters; and these are readily cyclised by dropping them into paraffin oil heated to 280° to 5-hydroxy-8 : 9-dimethoxy-1 : 2 : 3 : 4-tetrahydroacridine (VII) and 5-hydroxy-6 : 7 : 8-trimethoxy - 1 : 2 : 3 : 4 - tetrahydroacridine (VIII) respectively.

An attempt to apply the Döbner-Miller quinaldine synthesis to 3-aminoveratrole resulted in failure, and supplies of material were not available for further attempts.

Finally, it should be placed on record that attempts to prepare 6-carboxy-2 : 3-dimethoxyphenyl thioglycollic acid from 2-aminoveratric acid by diazotisation and coupling of the diazonium chloride with thioglycollic acid resulted in reduction of the starting material to veratric acid.

Experimental.

2-Methyl-4-hydroxy-7 : 8-dimethoxyquinoline (*III*).

3-Aminoveratrole (10 g.) was thoroughly mixed with ethyl acetoacetate (8·8 g.) and one drop of 5N hydrochloric acid was added. The mixture was then allowed to stand at room temperature. Water commenced to separate after a few minutes. After standing 3 days the oil was taken up, washed and dried in ether. After removal of the solvent the product was distilled *in vacuo*. Practically all (15 g.) distilled as a very pale green viscous oil boiling at 175-178°/2 mm. As this ethyl β-(2′ : 3′-dimethoxyanilino) crotonate did not crystallise it was heated to 100° and then added to paraffin oil (75 g.) preheated to 280°. A vigorous reaction ensued, and on cooling a solid separated. This was collected and freed from paraffin with the aid of petroleum ether. It was then crystallised from boiling water with the aid of decolorising charcoal. White needles, m.p. 212°, (yield 30%) were obtained.

Found : N=6·3% ; calculated for $C_{12}H_{13}O_3N$, N=6·4%.

The *picrate* of this base is readily obtained from alcoholic solution in yellow needles which melt at 230°.

Found : N=12·4% ; calculated for $C_{18}H_{16}O_{10}N_4$, N=12·5%.

2-Hydroxy-4-methyl-7 : 8-dimethoxyquinoline (*V*).

3-Aminoveratrole (5 g.) was added in one lot to ethyl acetoacetate (20 g.) previously heated to 145°. A vigorous reaction occurred and alcohol was split off. After maintaining the temperature at 140° for ten minutes, excess ethyl acetoacetate was removed *in vacuo* and the cooled oily residue was carefully dissolved in 8 times its weight of ice-cold sulphuric acid. The solution was allowed to stand for two hours, then poured into ice water and basified with ammonia. The precipitated solid was collected, dried and recrystallised from ethyl acetate. Yield 6 g. It melted at 175°.

Found : C=64·9, H=6·3% ; calculated for $C_{12}H_{13}O_3N$, C=65·8, H=6·0%.

5-Hydroxy-8 : 9-dimethoxy-1 : 2 : 3 : 4-tetrahydroacridine (VII).

3-Aminoveratrole (5 g.) and ethyl cyclohexanone-2-carboxylate (6 g.) were carefully mixed at room temperature and one drop of 5N hydrochloric acid added. Water commenced to separate after a few minutes. After standing for 24 hours the oil was taken up and dried in ether and the solvent removed. The residual oil did not crystallise. It was heated to 100° and then poured into paraffin oil (50 g.) previously heated to 280°. Alcohol was evolved and a brown oil separated which hardened to a brown resin on cooling. On freeing it from paraffin and washing with ether it crystallised, and was recrystallised from benzene. The substance was thus obtained in fine colourless needles, m.p. 212° (decomp.).

Found : N=5·5% ; calculated for $C_{15}H_{17}O_3N$, N=5·4%.

The yellow insoluble *picrate* of this base melted at 158°.

2-Methyl-4-hydroxy-5 : 6 : 7-trimethoxyquinoline (IV).

5-Aminopyrogallol trimethyl ether (2 g.) was mixed with ethyl acetoacetate (1·4 g.) and the mixture was heated at 100° until the base would no longer crystallise on cooling (about three hours). One drop of 5N hydrochloric acid was then added, and the mixture was allowed to stand for 24 hours. The oil was then dried in ether and after removal of the solvent was dropped into 6 times its weight of paraffin oil preheated to 280°. The solid which separated was freed from paraffin, washed well with ether and then recrystallised from alcohol. It came out in fine white needles, m.p. 198°.

Found : N=6·0% ; calculated for $C_{13}H_{15}O_4N$, N=5·9%.

2-Hydroxy-4-methyl-5 : 6 : 7-trimethoxyquinoline (VI).

5-Amino pyrogallol trimethyl ether (2 g.) was added to ethyl acetoacetate (10 g.) previously heated to 140°. A vigorous reaction commenced, and alcohol boiled off. After 10 minutes at 140° the excess ester was removed *in vacuo* and the cooled residue was dissolved in ice-cold concentrated sulphuric acid (20 g.). After 30 minutes the solution was poured into ice water and immediately basified with ammonia. The dirty precipitate which formed was collected and recrystallised from boiling water. It was thus obtained in fine colourless needles, m.p. 218°. Yield 2 g.

Found: C=62·4, H=5·9, N=5·9%; calculated for $C_{13}H_{15}O_4N$, C=62·6, H=6·0, N=5·9%.

The *picrate* of this base melts at 180°.

5-Hydroxy-6 : 7 : 8-trimethoxy-1 : 2 : 3 : 4-tetrahydroacridine (VIII).

5-Amino pyrogallol trimethyl ether (2 g.) and ethyl cyclohexanone-2-carboxylate (1·8 g.) were warmed together until solution was complete, one small drop of 5N hydrochloric acid was added and the mixture heated at 100° for 8 hours. It was then poured into 5 times its weight of paraffin oil at 280°, and after cooling, the oil which had separated from the paraffin crystallised. It was recrystallised from alcohol and was thus obtained in colourless needles, m.p. 200°.

Found: N=5·0%; calculated for $C_{16}H_{19}O_4N$, N=4·9%.

Attempt to prepare 6-carboxy-2 : 3-dimethoxyphenyl thioglycollic acid.

2-Aminoveratric acid (12 g.) was treated with concentrated hydrochloric acid (18 c.c.) and the mixture was cooled to 0°. A cold solution of sodium nitrite (4 g.) in water (20 c.c.) was then carefully stirred in, the temperature being kept below 2°. To the clear yellow diazo solution thus obtained, a solution of thioglycollic acid (6 g.) in water (20 c.c.) was added with vigorous stirring. The solution became red, but there was no precipitate. On allowing the temperature to rise nitrogen was evolved and a precipitate formed. Eventually the mixture was heated at 60° until gas evolution ceased. After cooling, the precipitated solid was collected and washed, then recrystallised from boiling water. The substance, which was an acid, came out in fine colourless needles melting at 182°. Yield 5 g.

Lassaigne's test indicated absence of sulphur from this substance. It was analysed.

Found: C=59·1, H=5·5%. Equivalent weight (by titration), 180.

These results all indicated that the substance was veratric acid $C_9H_{10}O_4$, calculated for which C=59·3, H=5·5%; equivalent weight, 182. A mixed melting point determination showed this to be so.

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HETEROCYCLIC COMPOUNDS DERIVED FROM CATECHOL ETHERS.

PART III. SYNTHESIS OF 1 : 2-DIMETHOXYACRIDINE.

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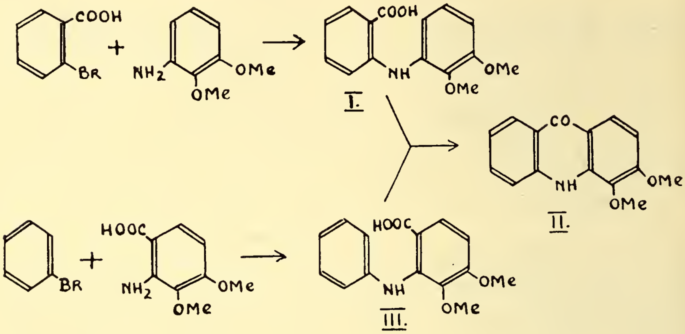
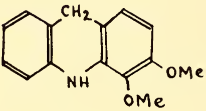
(*Manuscript received, September 22, 1937. Read, October 6, 1937.*)

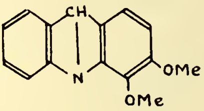
Borsche, Runge and Trautner (*Berichte*, 1933, *66*, 1315) have shown that 4-aminoveratrole can be condensed with 2-chlorobenzoic acid in presence of copper powder and potassium carbonate to give 3 : 4-dimethoxydiphenylamine-2′-carboxylic acid, which can be cyclised by means of phosphorus pentachloride to a mixture of 2 : 3-dimethoxyacridine and 2 : 3-dimethoxy-9-chloroacridine. These in turn can be reduced to 2 : 3-dimethoxydihydroacridine, which is readily oxidised to 2 : 3-dimethoxyacridine. We have now studied the preparation of 1 : 2-dimethoxyacridine and have been able to effect its synthesis from either 3-aminoveratrole or 2-aminoveratric acid, using methods similar to those described by Borsche and his co-workers.

Thus, 3-aminoveratrole condenses readily with 2-bromobenzoic acid in boiling amyl alcoholic solution in presence of copper powder and anhydrous potassium carbonate to give 2 : 3-dimethoxy diphenylamine-2′-carboxylic acid (I). Treatment of this acid with phosphorus pentachloride in carbon disulphide solution readily yields 1 : 2-dimethoxyacridone (II). Also, bromobenzene can be condensed with 2-aminoveratric acid in presence of copper powder and anhydrous potassium carbonate to 2 : 3-dimethoxy diphenylamine-6-carboxylic acid (III), and treatment of this acid with phosphorus pentachloride gives the acridone (III) in approximately the same yield as by the previous method. Reduction of (III) with sodium and absolute ethyl alcohol, according to the method of Ullmann and Maag (*Berichte*, 1907, *40*, 2516) leads to formation of 2 : 3-dimethoxy dihydroacridine (IV), a pale yellow crystalline substance of which solutions in alcohol show a vivid blue fluorescence. Oxidation of this dihydro base with chromic acid is readily effected with formation of 1 : 2-dimethoxyacridine (V), a solid which crystallises in pale yellow needles melting at 189°.





IV.



V.

EXPERIMENTAL.

2 : 3-Dimethoxydiphenylamine-2′-carboxylic Acid (I). 3-Aminoveratrole (5 g.) and o-bromobenzoic acid (6·8 g.) were dissolved in boiling amyl alcohol (30 c.c.), and copper powder (*Natur kupfer C*, 0·1 g.) and anhydrous potassium carbonate (5 g.) added gradually. The mixture was finally refluxed for 40 minutes. The amyl alcohol was then distilled off in steam, and the residue extracted with more boiling water, filtered, and acidified with hydrochloric acid. A black tar separated, which solidified after some minutes. It was repeatedly recrystallised from aqueous alcohol with the help of decolorising charcoal, and finally was recrystallised from benzene for analysis. It was thus obtained in colourless plates, m.p. 162°. Yield of purified material, 3·6 g.

Found : C=66·7, H=5·7% ; calculated for $C_{15}H_{15}O_4N$: C=65·9, H=5·5%.

2 : 3-Dimethoxydiphenylamine-6-carboxylic Acid (III) 2-Aminoveratric acid (5 g.) was heated under reflux with bromobenzene (30 c.c.) and copper bronze (0·1 g.) and anhydrous potassium carbonate (3·6 g.) gradually added. Refluxing was continued for two hours. Excess bromobenzene was then distilled off in steam and the residue taken up in boiling water, filtered, and acidified with concentrated hydrochloric acid. The brown precipitate which came down was collected and purified by recrystallisation from aqueous alcohol with the help of decolorising charcoal. It formed colourless needles m.p. 155°.

Found : N=5·5% ; calculated for $C_{15}H_{15}O_4N$: N=5·2%.

1 : 2-Dimethoxyacridone (II). This substance was prepared from both acids (I) and (III) by similar methods as follows : The acid (2·7 g.) was mixed with carbon disulphide (50 c.c.) and phosphorus pentachloride (2·1 g.) added. The mixture was then refluxed for two hours, during which time red crystals were deposited and hydrogen chloride was evolved. Eventually, the carbon disulphide was distilled off, and cold dilute ammonia added to the residual red solid. After trituration a yellow powder remained. It was recrystallised from aqueous alcohol, the yellow crystals melting at 225°. Solutions of this acridone in nitrobenzene or alcohol were yellow, and exhibited a marked green fluorescence.

Found : N=5·8% ; calculated for $C_{15}H_{13}O_3N$: N=5·5%.

1 : 2-Dimethoxydihydroacridine (IV). To a solution of 1 : 2-dimethoxyacridone (0·7 g.) in absolute ethyl alcohol (20 c.c.) metallic sodium (1·5 g.) was added. When the metal had dissolved excess alcohol was removed by evaporation and the filtered residue was diluted with water, when the dihydro base precipitated. It was recrystallised from alcohol and was obtained in pale yellow needles melting at 218°. Its alcoholic solutions show a vivid blue fluorescence.

Found : N=5·9% ; calculated for $C_{15}H_{15}O_2N$: N=5·8%.

1 : 2-Dimethoxyacridine (V). 1 : 2-Dimethoxydihydroacridine (0·3 g.) was treated with a solution of concentrated sulphuric acid (0·5 c.c.) in water (30 c.c.) and a solution of potassium dichromate (2 g.) in water (10 c.c.) added. The mixture was then heated on a rapidly boiling water-bath. After 10 minutes a clear green solution was obtained. This was filtered and basified with sodium hydroxide solution. The precipitate was collected and extracted with boiling alcohol, the alcoholic solution decolorised with charcoal and evaporated to a volume of approximately 1 c.c. On cooling the acridine separated in pale yellow needles which melt at 189°.

Found: $N = 5 \cdot 95\%$; calculated for $C_{15}H_{13}O_2N$: $N = 5 \cdot 9\%$.

The base readily forms a *picrate* in alcoholic solution. It can be obtained in yellow needles which melt at 220° with decomposition.

ACKNOWLEDGMENT.

The authors desire to express their grateful thanks to Miss E. M. Goulston, B.Sc., for some of the analyses recorded in this paper.

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NOTE ON THE EXUDATION OF ARAUCARIA BIDWILLI.

By Arthur John Birch, B.Sc.

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The exudation of *Araucaria Bidwilli* was briefly examined by Baker and Smith ("Research on the Pines of Australia", p. 369), who described it as possessing a slightly aromatic odour, but made no attempt to isolate any volatile oil from it.

Examination of a specimen of the exudation showed it to possess a strong, pleasant, lemon odour, and an examination was accordingly made for volatile oils. The specimen (collected in August) consisted of a mixture of viscous milky latex and brown translucent gum, produced from the lower portion of the tree as the result of accidental injury. The substance (100 grms.) was steam distilled until a litre of distillate had been obtained. This was then extracted with ether (100 c.c.), yielding 9·1 grms. of clear, colourless, mobile oil, possessing the pleasant odour of the original gum. The aqueous layer, which showed an acid reaction, was not further examined. The oil possessed the following physical constants:

$D_{4}^{16°}$ 0·8660 $\alpha_{D}^{18°}$ +102°·1 $N_{D}^{18°}$ 1·4765.

Distillation under reduced pressure gave the following fractions:

A.	B.p. 70°-80° C.	(22 mm.)	5 grms.
B.	B.p. 80°-112° C.	,,	0·5 grms.
	Residue		0·5 grms.

Fraction A. This was shown to consist essentially of *d* limonene by the preparation from it of the characteristic tetrabromide, m.p. 104° C., undepressed by admixture with an authentic sample. The β-nitrosochloride was obtained also, yielding carvoxime (m.p. 72°) by the action of alcoholic caustic soda.

Fraction B. This consisted of a pale yellow oil, somewhat more viscous than the preceding fraction, with a strong lavender odour. It gave no reaction with 2 : 4 dinitrophenylhydrazine sulphate, demonstrating the absence of aldehyde or ketone groups. A solution of methyl magnesium iodide in amyl ether gave a flocculent precipitate, but no gas was evolved, showing the absence of alcoholic groups, and the probable presence of esters or ethers. Owing to the small amount of material available no further examination was possible.

Gum. The residue from the steam distillation was filtered (with great difficulty), leaving a residue of dark brown resinous material (10 grms.) which was partly soluble in alcohol. The filtrate gave a flocculent precipitate on the addition of excess alcohol. This precipitate was filtered off and refluxed for a few minutes with concentrated hydrochloric acid, the mixture then being distilled. The distillate gave a strong test for furfural on the addition of aniline, indicating the presence of pentosans in the gum.

The very pleasant odour of the oil might render its commercial exploitation a possibility.

ACKNOWLEDGMENTS.

The author is indebted to the Commonwealth Government for a Research Scholarship, and to Professor J. C. Earl for advice.

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THE α-PHELLANDRENE FRACTION OF EUCALYPTUS OILS.

By Arthur John Birch, B.Sc.

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The purification of α-phellandrene is difficult, as it occurs in admixture with other substances of a similar boiling point; it is difficult to fractionate as it is polymerised by heating; and no solid derivative is known from which it can be regenerated. For these reasons the fractions which have been isolated from the leaf oils of many eucalypts, and identified as α-phellandrene by means of the nitrosite test, show a wide variation in their physical constants, especially their optical rotation, and are evidently far from pure. Smith, Carter and Read (*J.C.S.*, 1924, 932) quote examples of fractions possessing rotations varying from −5°·4 to −73°·8, and they assume the presence of *dl* α-phellandrene, although they were unable to isolate any derivatives of it. The α-phellandrene from these sources is always lævo-rotary, and these authors state that of the oils of 200 different species that they examined not one gave a dextro-rotary fraction. From this evidence the presence of *d* α-phellandrene seems very doubtful, especially as in many cases the *dl* compound would necessarily greatly predominate in order to give the observed rotation, and could hardly escape detection.

The chief difficulties hitherto encountered in the examination of these fractions have been the lack of methods for the detection of *dl* α-phellandrene in the presence of the optically active substance, and for the quantitative estimation of α-phellandrene, and for its removal to facilitate the examination of the other constituents. These difficulties, except the first, were overcome by an application of the "diene synthesis" by Birch (This Journal, 1937, *71*, 54) and this has now been solved by an extension of the method. It was found that admixture of the maleic anhydride addition compounds from dextro- and lævo-α-phellandrene lowered the melting point, as shown in the following table.

Dextro %	0	20	40	50	60	80	100
Lævo %	100	80	60	50	40	20	0
M.P.° C.	127	113	100	93	100	113	127

From this it is possible in the case of an unknown sample of α-phellandrene to determine the relative amounts of active and inactive substance present. The specific rotation of the addition compound could also be used to determine this, but it is less convenient to find, especially as it is low.

Application of these methods was made to a commercial sample of α-phellandrene, and to the α-phellandrene fractions of the oils of *Eucalyptus dives*, *E. radiata*, *E. risdoni*, and *E. amygdalina*.

The commercial sample was carefully examined, and was shown to contain no *dl* α-phellandrene, but to consist of a mixture of *l* α-phellandrene with a large amount of p-cymene, a small amount of some unidentified lævo-rotary terpene, and a little origanene. The occurrence of the latter is especially interesting, as it is the first recorded since its discovery by Pickles (*J.C.S.*, 1908, 868). Its structure is under investigation.

The other samples were less carefully examined owing to the smaller amounts available, but those from *E. dives*, *E. radiata* and *E. risdoni* were shown to contain a large percentage of p-cymene, and that from *E. amygdalina* a large amount of dipentene, while none of the oils contained *dl* α-phellandrene.

While a much larger number of cases must be examined before any general conclusions can be drawn, it seems likely from this evidence that the presence of p-cymene in α-phellandrene fractions in general provides at least a partial explanation of the variations observed in their physical constants. The characterisation of the phellandrene is easy, that of the p-cymene difficult, and accordingly fractions containing only relatively small amounts of α-phellandrene have been labelled as such. p-Cymene has already been noticed in commercial samples of phellandrene (Semmler, *Ber.*, *35*, 1750; Henry and Paget, *J.C.S.*, 1928, 72), but its significance has been missed. Dupont, Daure and Levy (*Bull. Soc. Chim.*, *51*, 923), have detected the occurrence of p-cymene in the α-phellandrene fraction of the oil of *Aucoumea Kleineanu burseracea* by an examination of the Raman spectrum. This phellandrene was relatively pure (α_{576}, +105°·2; $n_D^{15°}$, 1·4757; $D^{15°}$, 0·8430), having a higher rotation than the purest sample isolated by Smith, Hurst and Read (*J.C.S.*, 1923, 1662) from the oil of *E. dives*. Bodendorf (*Arch. Pharm.*, 1933, *271*, 1), by removal of the α-phellandrene as its peroxide from a fraction of α_D −89°·6, showed that it contained only 67% of the pure substance, and calculated the rotation of this to be −133°·25. The values obtained from the crude fractions of *E. dives* (−119°) and *E. radiata* (−108°) are somewhat lower than this value, probably owing to the presence of α-terpinene, but that from the purest α-phellandrene fraction (−133°) is in good agreement.

The p-cymene in the oil is probably derived from the α-phellandrene by the loss of two hydrogen atoms, and preliminary experiments have shown that it is probably the final result of atmospheric oxidation.

The presence of p-cymene in commercial α-phellandrene has some bearing on a recent paper by Dewar and Read (*J.C.S.*, 1936, 1781), who obtained a mixture of p-cymene and p-menthane by the action of metallic catalysts. As their starting product (α_D −67°·3) almost certainly contained a large percentage of p-cymene to begin with, the ratio of the products needs correction.

EXPERIMENTAL.

Mixed Melting Points of Maleic Anhydride Addition Compounds.

The addition product of *d* α-phellandrene was obtained from the terpene fraction of bitter fennel oil, and that of *l* α-phellandrene from the terpene fraction of *E. dives* oil. Both were recrystallised from alcohol. Solutions were prepared containing 1 gramme of substance in 10 c.c. of chloroform, and the solutions then mixed in the correct proportions to give the ratios of *d* and *l* forms shown in the table. These were allowed to evaporate, the crystalline residue well mixed, and the melting point taken. As the mixtures melted over a considerable range, the melting point shown is the temperature at which the last trace of solid material disappeared, the rate of heating for the last few degrees being about 2° per minute.

0·8739 gramme of addition compound from *d* α-phellandrene made up to 10 c.c. in chloroform gave a rotation of $+0^\circ\cdot45$ ($l=0\cdot5$), whence $[\alpha]_D^{16^\circ}=+10^\circ\cdot3$.

Examination of α-phellandrene Fractions.

The commercial sample of α-phellandrene was first extracted with 50% resorcinol to remove cineol, and with hot sodium sulphite to remove piperitone, and then fractionated through a nine bulb Golodetz column.

The following fractions were obtained.

	B.P.	Press.	R.I. 15°.	$\alpha_D^{15^\circ}$	Vol.	α-phellandrene.
		m.m.			c.c.	%
I	52°–55°	22	1·4648	−49°·0	30	58
II	55°–59°	22	1·4758	−89°·5	50	72
III	59°–60°	22	1·4776	−101°·0	105	80
IV	60°–62°	22	1·4815	−91°·5	185	72

Residue: 600 c.c.

Fraction III was then refractionated.

	B.P.	Press.	R.I. 15°.	$\alpha_D^{15^\circ}$	Vol.	$D\frac{12^\circ\cdot5}{12^\circ\cdot5}$
		m.m.			c.c.	
A	52°–55°	17		−68°·5	10	
B	55°–58°	17		−101°·0	7	
C	58°–59°	17	1·4760	−117°·4	35	0·8402
D	59°–60°	17		−114°·0	8	

Fraction C is evidently the purest, and an estimation showed it to contain 88% of α-phellandrene. It is the purest sample of lævo-α-phellandrene that has been isolated.

The residual oils obtained from fractions I-IV after treatment with maleic anhydride had the following constants:

	I.	II.	III.	IV.
R.I. 15°	1·4792	1·4814	1·4830	1·4850
$\alpha_D^{15^\circ}$	0·0	−2°·2	−0°·75	−0°·2

In order to study the other constituents of the oil, a purified α-phellandrene fraction B.P. 52°-70° C. (20 m.m.) was taken. The α-phellandrene was removed by means of maleic anhydride in acetone, and the residual oil fractionated under reduced pressure through a Golodetz column. The residue from 250 c.c. of fraction (105 c.c.) gave the following results :

	B.P.	Press.	R.I. 16°.	Vol.	$\alpha_D^{16°}$	Bromine Val.
		m.m.		c.c.		c.c.
I	60°–65°	23	1·4727	20	+4°·8	30
II	65°–67°	23	1·4878	50	−2°·8	17
III	67°–70°	23	1·4888	10	−3°·2	15
IV	70°–75°	23	1·4908	10	−2°·3	23

The solution of bromine used contained 4 grammes in 250 c.c. of glacial acetic acid, the volume shown being absorbed by 0·4 gramme of the fraction.

These fractions were then examined for their components.

Fraction I. This fraction readily yielded a crystalline nitrosochloride M.P. 90°–94° C., according to the rate of heating, which was converted into a nitrolpiperidine M.P. 197° C., and a nitrolbenzylamine M.P. 105°–106° C. These agree with the figures given by Pickles (*loc. cit.*) for the corresponding derivatives of origanene, 90°–94°, 198°, and 104°–105° respectively, and do not even approximate to those of any other known terpene.

Fractions II, III, and IV. No solid derivatives could be obtained from these fractions by the action of nitrous acid, nitrosyl chloride, or bromine, and they were shown to consist largely of p-cymene by the removal of unsaturated substances by means of 3% alkaline permanganate solution. The residual oil was then recognised as p-cymene by its physical constants, and by oxidation to p-(hydroxy-isopropyl) benzoic acid (M.P. 155°–156°) and terephthalic acid, with hot permanganate.

Fraction.	Residual p-cymene.		
	R.I. 16° C.	$\alpha_D^{16° C.}$	Percentage of Original Fraction.
II	1·4902	0·0	52
III	1·4900	−0·1	60
IV	1·4908	0·0	30

The α-phellandrene fractions of the following eucalypts were examined.

Eucalyptus dives. The fraction was treated with 50% resorcinol to remove a small amount of cineol, and with hot sodium sulphite to remove piperitone. It then had the following constants: $N_D^{13°}$ 1·4787, $\alpha_D^{13°}$ −81°·2. An estimation by means of maleic anhydride showed it to contain 69% of α-phellandrene, the residual oil having $\alpha_D^{15°}$ −1°·4, $N_D^{15°}$ 1·4850. This was shown to consist chiefly of p-cymene by the preparation of the characteristic p-(hydroxyisopropyl)benzoic acid (M.P. 155°–156° C.) by means of hot permanganate oxidation.

Eucalyptus radiata. After treatment with resorcinol and sodium sulphite this terpene fraction had the constants $N_D^{13°}$ 1·4778, $\alpha_D^{13°}$ −58°. It contained 54% α-phellandrene, and the residual oil had the constants $\alpha_D^{15°}$ −1°·3, $N_D^{15°}$ 1·4830. It was shown by oxidation to consist mainly of p-cymene.

Eucalyptus risdoni. This oil was treated several times with 50% resorcinol solution to remove large quantities of cineol, the resulting terpene fraction having the following constants: $N_D^{13°}$ 1·4780, $\alpha_D^{13°}$ −24°·8. This was treated with maleic anhydride and the residual oil shown by oxidation to the characteristic acid to be p-cymene.

Eucalyptus amygdalina. The terpene fraction of this oil was treated with 50% resorcinol to remove much cineol, then having the constants $N_D^{16°}$ 1·4780, $\alpha_D^{16°}$ −10°·0. The oil left after treatment with maleic anhydride had $\alpha_D^{16°}$ −0°·5, $N_D^{16°}$ 1·4815, and possessed a lemon odour. It was shown to consist largely of dipentene by the preparation from it of the characteristic tetrabromide, M.P. 124°–125° C.

The maleic anhydride : α-phellandrene addition compound from each of these oils was carefully recrystallised from ethyl alcohol, but in no case could a crystalline fraction be isolated having a melting point lower than 125° C., thus proving the absence of any *dl* α-phellandrene.

ACKNOWLEDGMENTS.

The author wishes to express his thanks to the Commonwealth Government for a research scholarship, and to Messrs. Thomas and Cameron, of Mortlake, for a gift of *E. dives* oil.

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THE GEOLOGICAL STRUCTURE AND STRATIGRAPHY OF THE MOLONG-MANILDRA DISTRICT.

By GERMAINE A. JOPLIN, B.Sc., Ph.D., and ALMA G. CULEY, M.Sc.

(With Plate II and one text-figure.)

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CONTENTS.

I. INTRODUCTION AND PREVIOUS RECORDS.

Molong and Manildra are situated on the Broken Hill Railway line at distances of 224 miles and 239 miles respectively from Sydney.

The district mapped lies between Molong on the east and Manildra on the west, and extends in a north-south direction for about 20 miles. The area measures about 300 square miles.

In the past this district attracted attention because of the occurrence of small deposits of gold, copper, tin, bismuth, and molybdenum, and brief geological reports have been made by Wilkinson,[(13)] [(14)] Anderson,[(1)] and Carne.[(6)] [(7)] Limestones are extensively developed in the eastern part of the area, and these have been reported upon by Carne and Jones. The district has been briefly described and correlated with other areas by Sussmilch[(12)] and by David.[(9)]

In the present paper the limestones and their associated beds have been subdivided into Silurian and Middle Devonian, and the Silurian strata have been divided into an upper and lower series, as indicated in the following summary of the stratigraphy.

Period.	Beds.	Rock Types.	Approximate Thickness.
			Feet.
Recent ..		Alluvium, gravel, ferruginous sandstone and conglomerate.	
Tertiary ..		Laterite, drift deposits (auriferous).	
Devonian—			
Upper ..	Lambie.	Grits, conglomerates, sandstone, red shales.	1,600 –
Middle ..	Garra.	Limestones, clay-slates, tuffs, quartzites.	4,000 –
Silurian ..	Manildra.	Tuffs, cherts, clay-slates.	3,000 +
	Molong.	Limestones, clay-slates, etc.	3,000 +

II. General Geology.

A. Sedimentary.

(i) Silurian.

(*a*) *Molong Beds.* Reference to the map (Plate II) and sections (Fig. 1) will show that the Molong Beds form the lowest division of the Silurian in this district. They crop out in a general north-south belt through Molong, and again in the south-west near Gregra. To the west they are immediately overlain by the Manildra Beds, which are also of Silurian age, and together with the upper beds they are thrown into a series of folds trending a little to the west of north. Carne and Jones ([(8)] p. 169) have mapped an anticline in them, the axis of which passes through the town of Molong. It was formerly believed that the Bocoble Creek limestone was on the same horizon as that of Molong, the beds forming a syncline between the two localities. We now believe that the Bocoble Creek limestone is of Middle Devonian age, and that this and the overlying Upper Devonian have been preserved in a synclinal structure.

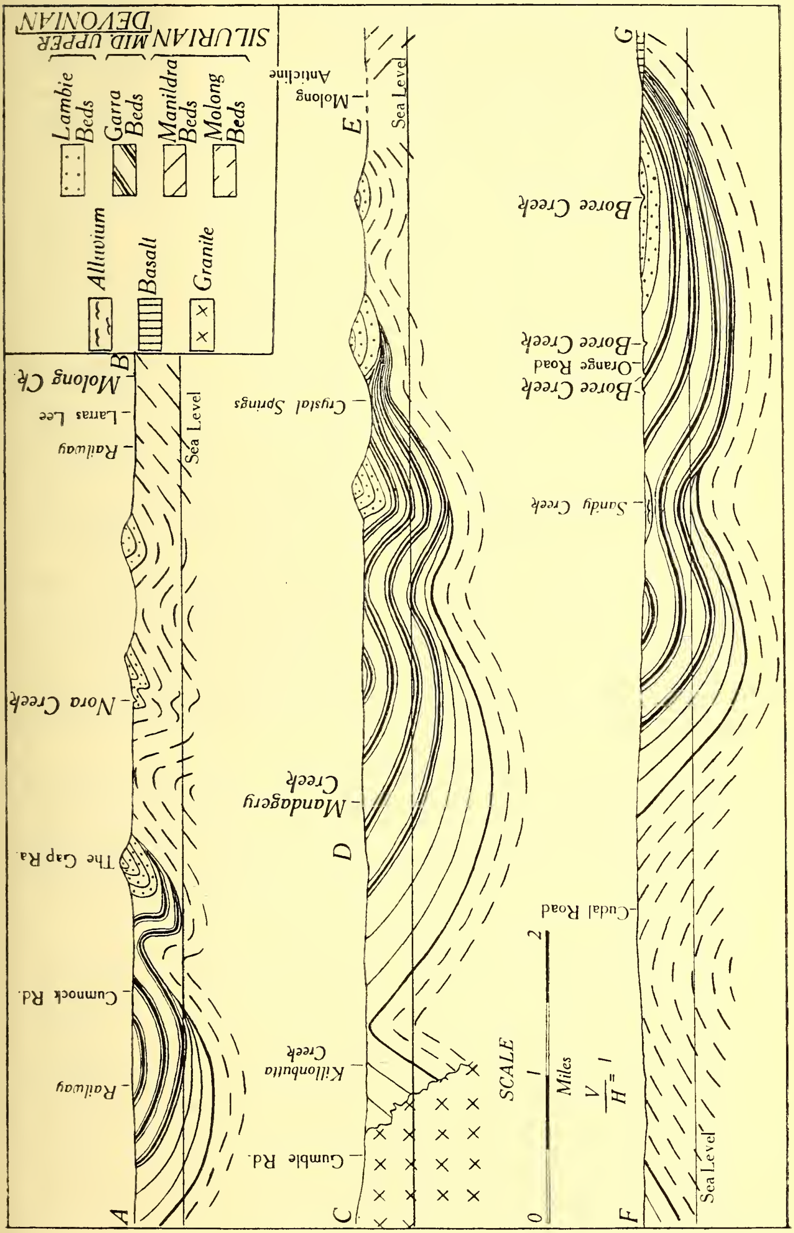
Lambie Beds
Garra Beds
Manildra Beds
Molong Beds
UPPER
MID.
DEVONIAN
SILURIAN
Alluvium
Basalt
Granite
A
B
Molong Ck.
Larras Lee
Railway
Sea Level
Nora Creek
The Gap Ra.
Cumnock Rd.
Railway
C
D
E
Molong Anticline
Sea Level
Crystal Springs
Mandagery Creek
Killonbutta Creek
Gumble Rd.
SCALE
0
1
2
Miles
V/H = 1
F
G
Boree Creek
Boree Creek
Orange Road
Boree Creek
Sandy Creek
Cudal Road
Sea Level

Fig. 1.

The Molong Beds consist of limestones and shaly beds, which are altered and are of the nature of clay-slates. In the town of Molong and to the east contemporaneous lava flows occur, but these have not been mapped. The clay-slates are usually interbedded with the limestones, but owing to their much jointed and fissile nature they give poor outcrops. As a rule they are unfossiliferous.

Limestones form very prominent outcrops in the town of Molong and to the south along the Cudal Road. Other fairly extensive outcrops associated with clay-slates occur along the Cudal Road south of Gregra Platform, and they are again met with on the main Manildra-Cudal Road near the Cudal Trig. Station. In the northern part of the area massive limestones are developed on Nora Creek, and in the angle between the road and railway line, Por. 102, Par. The Gap, the Upper Devonian beds occupy a synclinal trough within the Silurian limestone. Limestones also crop out in a southern tributary of Nora Creek, Pors. 109, 130, Par. The Gap. On certain horizons the limestones are highly fossiliferous, but we have not made extensive collections in this series.

Amongst the fossils noted are: *Tryplasma lonsdalei* var. *scalariformis* Eth. fil., *T. liliiformis*, *Cyathophyllum* sp., *Favosites* spp., *Syringopora* sp., *Pachypora* sp., *Heliolites* sp., *Halysites* spp. (particularly abundant in Por. 81, Par. Gregra), Stromatoporoid, *Conchidium knightii*, Gastropods, *Atrypa reticularis* Linn., *Atrypoidea australis* Mitchell and Dun, and cf. *Ophidioceras* sp.

The Molong Beds give rise to gently undulating country which is extensively cultivated. Around the town of Molong numerous vineyards flourish on the calcareous soil. The cultivation has caused difficulties in tracing continuous limestone horizons and in mapping geological boundaries. Reference to the map will show that these boundaries have been indicated only by dotted lines.

(*b*) *Manildra Beds*. This series is typically developed around Manildra. It consists of tuffs, cherts, and much jointed indurated shales and forms a north-south belt to the west of the Middle Devonian Series, which overlies it conformably. To the west the beds attain a thickness of approximately 3,000 feet, and they thin out rapidly to the east. They do not appear to overlie the Molong Beds on the eastern side of the Middle Devonian belt, but a small outcrop occurs in the south part of the area where an anticline in the Silurian has been eroded.

Reference to the map may suggest that an unconformity exists between the Silurian and Middle Devonian in the southern part of the area, but this does not appear to be the case. In the first place, owing to cultivation, mapping has been difficult and it is possible that a narrow strip of the Manildra Beds may be developed along the western margin of the Middle Devonian. Secondly, it is possible that the tuffs have an irregular boundary and extend a little further to the east in the southern portion of the area. In a creek, Por. 3, Par. Cudal, excellent evidence of the conformity of these beds with the Middle Devonian may be seen, and the same conformable relation is shown in Killonbutta Creek, Por. 31, Par. Bell.

On Mandagery Creek, below the junction with Gumble Creek, cherts, forming resistant bands across the stream, are the predominating types in this series, though tuffs and jointed shales occur. In fact the cherts appear to pass imperceptibly into tuffs on the one hand, and into shales on the other. It is thought that some of the cherts may be extremely fine-grained tuffs. The massive cherts are deep greyish-blue in colour and have a subconchoidal fracture. Well defined banding is usually present and there is often evidence of silicification. A small mass of basic igneous rock occurs associated with the cherts in Pors. 6 and 61, Par. Gumble. This has not been examined in detail, but may represent either an interbedded flow or a Tertiary capping.

The shales, when fresh, are dark olive green in colour but readily weather to a buff shade. On account of their incompetence they are much fractured and sheared, and therefore often appear older than the tuffs and cherts with which they are interbedded.

Around Manildra tuffs are the predominant members of the series and this is possibly due to their proximity to the centre of volcanic activity. Here coarser types of breccia are developed and massive outcrops of large rounded boulders occur, not unlike outcrops of a plutonic rock. The breccias are often fossiliferous, and four miles south of Manildra, Por. 52, Par. Cudal, *Mucophyllum* sp. and *Dalmanites* have been collected. The texture of the tuffs is very variable, there being all gradations from the coarse breccia type into extremely fine tuffaceous shales. On Manildra Creek and in a tributary creek in Par. Manildra, Pors. 71 and 70 respectively, fossils have been found in the tuffs and shales. While very abundant, the forms occurring in the fissile shales are somewhat flattened. *Tryplasma lonsdalei* var. *scalariformis* Eth. fil., *Favosites* sp., crinoid stems and small brachiopods have been collected. The tuffs and breccias are of a dark greenish colour, but give rise typically to a deep red soil. They may show spheroidal weathering, and this is particularly noticeable when they are interbedded with the more resistant cherts.

Both breccias and fine tuffs are interbedded with the cherts and shales, but a tuff of medium texture is a predominating type. On account of discontinuous outcrops and the great variability in the width of the bands, it is impossible to give an estimate of the relative abundance of tuff and chert in the area. Individual tuff bands vary from one inch to many feet in thickness. Around Manildra the tuffs are invaded by small masses of granite-porphyry.

Under the microscope the tuffs are seen to be typically clastic rocks, made up almost entirely of igneous material. Rock fragments are often present, these being trachytes, rhyolites, quartzites, or devitrified glass; trachyte fragments are the most common. Mineral grains are also very abundant—albite, quartz, diopside, and iron ores having been recognised in the coarser tuffs. The albite is often subidiomorphic and may measure up to 2 mm. Quartz crystals usually show corrosion and may be bordered by a secondary deposit of silica—sometimes in the form of chalcedony. Calcite is very abundant in most of the tuffs, but this appears to be associated in every instance with organic structures. The rocks show a good deal of alteration, which is evidenced by the presence of epidote, clinozoisite, chlorite, sericite, and in a few cases by a little incipient biotite. Some of these materials—notably the biotite and epidote—may be accounted for by the subsequent metamorphism of the tuff by granite, and indeed some of the rocks show slight recrystallization and the development of minute granules in and around mineral fragments. There seems little doubt, however, that aqueous solutions have played an important part in the development of chlorite, chalcedony, and some epidote, and it is possible that these may have been associated with the initial ejection of tuff or with the metasomatic phase of the granite.

(ii) Devonian.

1. Middle Devonian.

(*a*) *Garra Beds.* The Garra Beds of the Middle Devonian Series occur immediately above the Manildra Beds on the west and are overlain by the Upper Devonian Series on the east.

These beds lie in a north-south belt about 2½ miles west of Molong and have been mapped for a distance of 20 miles from Cudal on the south, through Garra and Crystal Springs to beyond Nora Creek on the north. The width of the belt averages about 2½ miles.

As previously stated (p. 270) these beds are conformable with the Upper Silurian and thus occur in a series of north-south trending folds. In the northern part of the area folding is more intense and vertical dips are not infrequent. Like the Manildra Beds the Garra Beds thin out to the east and are not developed on the eastern margin of the Upper Devonian belt. A possible exception occurs on Boree Creek, where rocks, which are believed to be of Middle Devonian age, immediately underlie the Upper Devonian conglomerates on their eastern margin.

The Garra Beds consist of rhythmically banded limestones, calcareous shales, fissile clay-slates and subordinate tuffs, cherts and quartzites.

The limestones are generally dark grey and are intercalated with the calcareous brachiopod-bearing shales. A single limestone bed may vary in thickness from a few inches to several feet. Brecciation and rhythmic banding are characteristic and in these beds fossils are very numerous (see Table 1).

The calcareous shales vary as to lime content, and may sometimes be regarded as impure limestones. They are usually of a greyish-purple colour. The calcareous shales may be interbedded with the massive limestones or with the clay-slates. Brachiopods are more abundant in the shales than in the limestones, and reference to Table 1 will show where these occur.

The clay-slates are particularly well developed in the Nora Creek area and to the south on Boree Creek, though they may occur elsewhere, but owing to their highly fissile nature do not form prominent outcrops.

The quartzites, tuffs and cherts are not well developed but have been noted near Nora Creek, Pors. 191, 194, Par. The Gap, on Mandagery Creek, Por. 73, Par.

TABLE 1.

	Cudal.		Garra.				Crystal Springs.			
			Par. Brymedura.							
	Por. 3, Par. Cudal.	Por. 3, Par. Gregra.	Por. 32.	Por. 77.	Por. 73.	Por. 31, Par. Gumble.	E. limb. Pors. 108, 124, 174. Par. Bell.	W. limb. Pors. 81, 27, 177. Par. Bell.	Nora Ck. Pors. 99, 93, 191, 36, 82. Par. The Gap.	Gap Ck. Por. 52, Par. The Gap.
Receptaculites australis	x	x		x	x		x	x	x	x
Tryplasma princeps Eth. fil. ..	x		x	x	x		x	x	x	x
T. liliiformis		x		x			x	x	x	x
T. spp.	x					x	x	x		
Cyathophyllum spp.			x				x		x	
Diphyllum sp.			x						x	
Spongophyllum sp.			x							
Rhizophyllum enorme Eth. fil.	x(10)		x		x				x	
Cystiphyllum spp.	x	x	x	x	x		x		x	
Favosites spp.	x	x	x	x	x	x	x	x	x	x
F. cf. *salebrosa* Eth. fil. ..	x						x			
F. basaltica var. *moonbiensis* Eth. fil.		x							x	
Syringopora spp.	x	x	x	x	x	x	x	x	x	x
Pachypora sp.		x	x	x			x		x	
Heliolites spp.	x	x	x				x	x	x	x
Stromatoporella sp.						x				
Stromatoporoids	x	x	x	x	x	x	x	x	x	x
Crinoid stems	x	x	x				x	x	x	x
Orthis striatula (?) Schlotheim ..							x		x	
Leptæna rhomboidalis Wilkins ..			x		x			x	x	
Strophomena sp.					x					
Chonetes sp.			x	x			x		x	
Pentamerus sp. cf. *sieberi* von Buch									x	
Rhynchonella cf. *wilsoni* Sowerby					x					x
Atrypa reticularis Linn. ..					x				x	
A. sp.					x				x	
Spirifer sp.					x					
Meristella sp.					x					
Loxonema sp.	x		x	x		x	x			
Euomphaloid		x	x				x			
Orthoceras sp.		x		x			x	x	x	
Actinoceras sp.									x	

Brymedura, and on Killonbutta Creek, Por. 31, Par. Bell. It seems evident that the tuffs and cherts are developed only at the base of the Garra Beds. The tuffs are less massive than those of the underlying Manildra Beds and are associated with narrow bands of fossiliferous shale and limestone.

It is hoped that detailed palæontological work on the fauna of the Garra Beds will be carried out later.

2. Upper Devonian.

(*a*) *Lambie Beds.* The Upper Devonian beds developed in this area are typically Lambie Stage(3) and therefore form the upper part of the Upper Devonian Series.

The beds occur in a north-south belt trending along a prominent ridge from Cabonne Trig. Station on the south to Molong Trig. Station on the north. Beyond this point the country is more dissected and the belt extends intermittently further north for a distance of five miles. Small outliers form ridges west of the main belt in the Pars. Brymedura and Gregra (see Plate II). The belt is 2½ miles in width and the ridges rise to some 350 feet above the surrounding country. The Lambie Beds occur in a series of north-south trending folds and conformably overlie the Garra Beds, which thin out to the east, resulting in an overlap of the Upper Devonian on the Silurian.

These beds are preserved in a series of synclines, but minor folding is frequent, as shown along the railway line, Por. 103, Par. Brymedura, on the Parkes Road, between Pors. 152 and 205, Par. Brymedura, and on the Cumnock Railway line, Por. 95, Par. Bell. In the northern part of the area the folding is more intense, and small overfolds, vertical dips, and slickensides have been noted. In Por. 102, Par. The Gap, a small tributary of Nora Creek reveals a syncline of Lambie strata folded into the Silurian limestone. The thickness of the Upper Devonian Series has been estimated at about 1,600 feet, but this may be excessive owing to the minor folding.

The most prominent rock type developed in this series is a coarse grit usually of a reddish colour, in many cases showing banding and current-bedding. Jointing is well developed, and weathered tors give rise to very rugged outcrops.

Red or purplish-red shales are also well developed in the Lambie Beds, and, these being incompetent beds, are much crumpled and usually give rise to " biscuity " outcrops. Owing to close jointing the beds often appear to be vertical (see Brown and Joplin),* but the true dip may be determined from the interbedded sandstones.

Red sandstones and sandy shales also occur, and the finer varieties show ripple-marks on many horizons. These are well exposed in the railway cutting, Por. 103, Par. Brymedura, and on the Parkes Road. Massive conglomerates are present at the base of the series on Mousehole

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* In MS.

Creek in the south-east corner of the area. These conformably overlie the Garra Beds and a good exposure may be seen in the creek. Conglomerates have also been noted on the Cumnock railway cutting, Por. 95, Par. Bell.

Owing to lack of clearing the Upper Devonian belt stands out in contrast with the more fertile surrounding country. On this belt *Callitris calcarata* (Black Pine) and *Casuarina stricta* are very characteristic. There is a cultivated gap in the Upper Devonian along the railway line near Pinecliff, and the presence of vineyards suggests a calcareous soil. It seems evident that either Silurian or Middle Devonian limestones are present at no great depth and it is likely that only a veneer of Lambie strata occurs in this area.

(iii) The Geological Age of the Palæozoic Series.

The Silurian has been divided into a lower (Molong) and upper (Manildra) series. *Halysites* sp., *Conchidium knightii* and *Atrypoidea* sp. occur in the Molong Beds and these are regarded as typical Silurian forms. The three genera are to be found in the Silurian of Yass, which has been correlated with the Yeringian of Victoria and with the Wenlock of Britain.(9) The Manildra Beds are regarded as Silurian on account of the occurrence of *Mucophyllum* sp. and *Dalmanites* sp.

A Middle Devonian age has been assigned to the Garra Beds on palæontological grounds and on account of their stratigraphical position.

Receptaculites australis is a common type in the Murrumbidgee Middle Devonian province, whilst *Meristella* sp. and *Stromatoporella* sp. are characteristic forms in the Devonian of the Northern Hemisphere. *Tryplasma princeps*, with all other members of that genus, was referred to the Silurian by Etheridge,(11) but later Benson(2) found this species in the Middle Devonian limestone of Tamworth and Dr. Ida Brown(5) recently found it on Cave Island, Murrumbidgee River. The localities for this genus cited by Etheridge are either from the Tamworth district or from the Molong-Manildra area, and it is likely that this form was described with Silurian collections before the Silurian and Devonian were differentiated. From the foregoing lists it is clear that very different assemblages occur in the Silurian and Middle Devonian of the Molong district.

In the near future we hope to extend the geological mapping further north, towards Wellington, where Miss

Elizabeth Basnett has recently discovered *Rhizophyllum enorme*,⁽⁵⁾ and until this work is complete it is premature to attempt correlations and palæontological comparisons with other localities of Middle Devonian age.

An Upper Devonian age is assigned to the grits, conglomerates, and red shales overlying the Garra Beds on account of their marked resemblance to typical Lambian rocks as developed in the type-area at Mt. Lambie and on the South Coast of New South Wales.⁽³⁾

(iv) Tertiary and Recent.

At intervals along the Gumble-Molong Road through " Killonbutta ", small patches of ferruginous gravel occur. Elsewhere in the district, notably along Mandagery Creek and Nora Creek, drift deposits of Tertiary age are found to be auriferous.⁽¹⁴⁾ Ironstone cappings—possibly of Tertiary age—are met with to the north of Crystal Springs at intervals along the Nora Creek Road, and pisolitic laterite occurs in isolated patches in Pors. 27, 99, Par. Bell.

In many parts of the district, particularly along the course of Mandagery Creek, at Crystal Springs, there is very extensive gullying, and in this creek masses of conglomerate and sandstone occur at depths of about ten feet from the surface. The rocks are completely consolidated and in places form the bed of the creek. Some of the conglomerates are extremely coarse and seem to represent cemented masses of stream gravels. The cement is often ferruginous but may be argillaceous and the deposits may be due to exsudation during a cycle of alternating wet seasons and drought.

In the banks of Manildra Creek sandstones and conglomerates occur at about four feet to five feet from the surface and at about three feet above the present level of the stream. It would seem evident that these deposits are recent, and they probably represent a former level of the creek.

Throughout the district river terraces about five feet above the present stream level are developed and these consist mainly of gravels. On Manildra Creek and on Boree Creek alluvium and gravels cover fairly extensive areas.

B. Igneous.

(i) Rhyolites.

Rhyolites occupy the western part of the district mapped and it is known that they extend as far west as Bocobra

Creek. On the eastern side the rhyolites extend a few chains east of the Gumble road, where they are cut off by granite. Further south, in Por. 109, Par. Manildra, the Silurian sediments appear to dip beneath the rhyolites, but the junction is obscured by cultivation and again further south by the alluvium and gravels of Manildra Creek.

Manildra Creek and its tributaries dissect the rhyolite mass, which gives rise to rough and rugged country, with numerous bold outcrops. Around Gumble, however, in the area drained by Bray's Flat Creek the country is more mature, terraces of gravel are numerous and rhyolite outcrops infrequent. It is possible that this different type of country may be due to a change in the nature of the rhyolite. The rhyolite country is thickly wooded and *Callitris calcarata* (Black Pine) is very abundant. The area is poorly settled and has not been cleared.

The rhyolite series includes a number of types varying from a fairly coarse quartz-porphyry to a very fine felsitic rock. Fluidal fabric is often well developed, and in the more compact felsitic types this is displayed only on the weathered surfaces. The banding affords the only means of ascertaining the general trend of the rhyolites. Platy parting is often developed and occasional columnar jointing has been noticed. In Pors. 7, 20, 168, Par. Manildra, spherulitic rhyolites crop out. The spherules vary in size from 0·5 mm. to 15 mm. in diameter. It is possible that these lavas represent devitrified obsidians. In places brecciated rhyolites occur.

The petrology of this series has not been studied, but it is obvious that there has been some differentiation, and that slightly more basic types are interbedded.

On account of obscured relations at the margins of this formation its geological age is not directly determinable, but apparently the westerly dipping Upper Silurian Series to the east underlies the rhyolites. This would place the volcanic series either in the upper part of the Silurian or in the Devonian.

Considering this in the light of known occurrences of rhyolites elsewhere in eastern Australia, we think it probable that the rhyolites are of either Lower or Middle Devonian age.

(ii) Granite.

The granite has not been studied in any detail either in the field or in the laboratory.

Reference to the map will show that in addition to the main Gumble mass several smaller masses crop out near Manildra. These latter are more numerous than is indicated, but the small scale of the map prevents their inclusion. The granites are mainly acid types, and the masses to the south are of the nature of granite-porphyry, and are probably apophyses of the main boss. Dykes are very numerous on the north-east margin of the Gumble mass and quartz-felspar-porphyries, porphyrites, aplites, pegmatites, and more basic types have been recognised.

Gold, copper, tin, molybdenum, and bismuth are associated with the granite in small amount, and numerous small shafts are to be found along the contact zone, where interesting hornfelses and metasomatic types are developed.

(iii) Basalt.

In the south-east of the area, north of Cudal, large outcrops of basalt occur. These are probably of Tertiary age, but have not been examined by us.

III. Structure and Geological History.

The foregoing discussion on the stratigraphy indicates that the conditions of sedimentation did not differ widely from Silurian to Middle Devonian times. Limestones and fine sediments are found in both. The Silurian period closed with great outpouring of volcanic tuff and minor volcanic activity also took place in early Middle Devonian times. There is no angular break between these two systems, but the absence of the Lower Devonian suggests a non sequence. It is possible that the Gumble rhyolites are Lower Devonian flows, but these do not occur on the east, where the Manildra and Garra beds are adjacent and conformable. Detailed palæontological work may make it possible to divide the Garra Series into Lower and Middle Devonian strata, but so far as is known at present the Lower Series appears to be absent.

Middle Devonian sedimentation was followed by a remarkable change of facies, and the arenaceous types of the Upper Devonian were laid down, again without any angular break upon the Middle Devonian limestones and shales. An erosional break, however, is indicated by the overlap of Upper Devonian on Silurian. (See p. 275.)

Dr. Ida Brown⁽⁴⁾ has drawn attention to the change of facies between the Upper and Middle Devonian in parts of New South Wales and in Victoria and has pointed out that an unconformity exists. In the Molong area, however, there is no evidence of such a break, and as indicated above (p. 275), there is field evidence to show that the Upper Devonian is structurally conformable with both the Middle Devonian and the Silurian.

Diastrophism occurred during the Kanimbla Epoch, and no folding occurred until the close of Upper Devonian time. Reference to the map (Plate II) will show that Silurian, Middle Devonian, and Upper Devonian strata all trend slightly to the west of north, and have been folded together. Minor folding is common in all three series and transverse flexing is clearly indicated. Intense folding is developed locally and in the northern part of the area vertical dips are recorded.

The following table shows the sequence of the main geological events of the Molong-Manildra district.

TABLE 2.

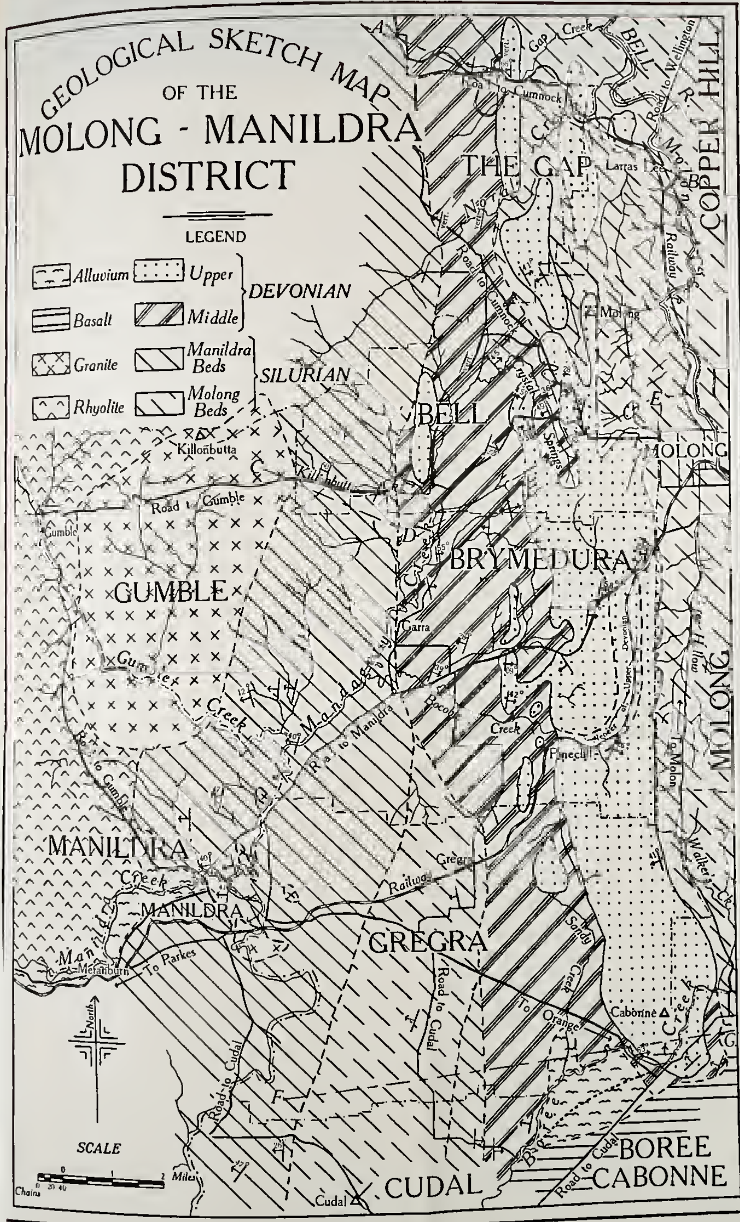
Summary of Geological History.

Silurian	Molong Beds	Deposition of limestones, shales, etc.
	Manildra Beds	Ejection of tuffs into shallow seas and deposition of shales on a steadily subsiding sea-floor.
	Non sequence.	
		? Outpouring of rhyolitic lavas.
Middle Devonian	Garra Beds	Deposition of tuffs, limestones and shales.
	Non sequence and change of facies.	
Upper Devonian	Lambie Beds	Deposition of conglomerate, grits, red sandstone and shales.
	Epoch of Diastrophism.	
		Intrusion of Gumble and Manildra granite.
	Uplift and Erosion.	
Tertiary		Formation of drift deposits, laterites, etc.
	Erosion.	
Recent		Formation of present stream channels, deposition of alluvium, gravels, etc.

IV. ACKNOWLEDGMENTS.

We gratefully acknowledge the generous help of Dr. Ida Brown, to whom we are indebted for fossil determinations and for helpful discussion on palæontological problems.

J


GEOLOGICAL SKETCH MAP
OF THE
MOLONG - MANILDRA
DISTRICT
LEGEND
Alluvium
Basalt
Granite
Rhyolite
Upper
Middle
DEVONIAN
Manildra Beds
Molong Beds
SILURIAN
A
Gap
Creek
BELL
R.
Road to Wellington
COPPER HILL
Road to Cumnock
THE GAP
Larras Lee
Molong
Railway
Road to Cumnock
BELL
Crystal
Springs
MOLONG
Killonbutta
Killonbutta
Cr.
Road to Gumble
Gumble
GUMBLE
Gumble
Creek
D
Creek
BRYMEDURA
Garra
Mandagery
Road to Manildra
Boco
Creek
Pinecliff
Upper Devonian
To Molong
MOLONG
Road to Gumble
MANILDRA
Creek
MANILDRA
E
Gregra
Railway
Walker's Ck
GREGRA
Road to Cudal
Sandy
Creek
To Orange
Cabonne
Creek
G
Manildra
Meranburn
To Parkes
North
Road to Cudal
F
Boree
Road to Cudal
BOREE
CABONNE
SCALE
0
1
2 Miles
Chains
Cudal
CUDAL

During the field work we were accompanied on two occasions by Miss Una Pickard, B.Sc., and on one occasion by Misses Basnett, Breckenridge, and Johnston, and to all we record our thanks.

We also acknowledge the assistance of Miss G. Carey, M.Sc., in determining certain trees in our area.

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THE CAUSES OF ICE AGES.

DISCUSSION OF PAPER BY G. H. HALLIGAN, F.G.S.

By Dr. E. Kidson.

(*Manuscript received, August 30 1937. Read (by title only), October 6, 1937.*)

In the Journal and Proceedings of the Royal Society of New South Wales, Vol. LXX, pp. 225-256, appears a paper on " The Causes of Ice Ages " by Gerald H. Halligan, F.G.S. His main conclusion is that " from what has been written, we must, I think, admit that no salient fact has been brought forward which vitiates the conclusions arrived at by Dr. J. J. Croll forty-five years ago and set out in such a careful, lucid, exhaustive, and conclusive manner in ' Climate and Time ' and the companion volume ' Climate and Cosmology ' ". The list of references given at the close of the paper and the whole tenor of his arguments suggest that the author is not familiar with modern developments in either meteorology or hydrography. We are still far from being able to give a complete and satisfactory explanation of the climatic changes of the past but our knowledge of the processes of the atmosphere and the hydrosphere have increased enormously since Croll's time, and it is no disparagement of his work to say that it is now easy to prove that much of his reasoning was unsound. It would be entirely out of place here and would take far too much space to criticize Croll's work at all fully, but in view of Mr. Halligan's wholesale adoption of his arguments and conclusions it seems desirable to expose their weaknesses in some detail.

After a brief exposition of the geological facts that have to be accounted for, Mr. Halligan discusses the " Fundamental Astronomical Facts " on the lines followed by Croll. The phenomena he is especially concerned with are the precession of the equinoxes and the variation of the eccentricity of the earth's orbit. At times of maximum eccentricity the distance between the sun and the earth will vary in the course of the year between 98·5 and 84·3 million miles, approximately. The amounts of radiation received from the sun at these distances will be in the ratio of 19 to 26. The effect of precession will be that at periods of maximum eccentricity the northern hemisphere will sometimes have its summer in perihelion and sometimes the conditions will be reversed. According to the amount of heat received from the sun, if the northern summer is in perihelion, it should be short and hot and the winter long and cold. The southern hemisphere, meanwhile, would have a long, cool summer and a short, mild winter. Other things being equal, there would then be a much greater contrast between summer and winter in the northern than in the southern hemisphere. (Halligan's statement on page 230 that "in this case the difference between summer and winter in the latitude of England would be almost annihilated" is an obvious slip, but this and a similar reversal of the argument on the following page make the paper very difficult to read.) It is contended that this state of affairs will "tend to produce glacial conditions upon one hemisphere and genial to hot conditions on the other". But since the total amount of heat received from the sun in the course of the year by either hemisphere is practically constant, whatever be the conditions as regards eccentricity or precession, the reason for this is not obvious.

Nor is it clear why the average position of the median line between the trade winds should be either north or south of the equator as is inferred in the first part of the following section on "Fundamental Physical Facts". Under the conditions we have assumed the effect of solar radiation would be to produce a greater contrast of temperature than normal between pole and equator in winter in the northern hemisphere. This would intensify the trade wind in that season but in summer the situation would be reversed and the average strength may still be the same as when the eccentricity was small and equal to that of the trade in the southern hemisphere. If one accepts Croll's conclusion that the northern hemisphere would become colder than southern, then it could perhaps also be granted that the north-east trade would blow across the equator. At the present time, the southern hemisphere has its summer in perihelion and its average temperature is lower than that of the northern: the south-east trade, also, extends into the northern hemisphere as would be expected from Croll's theory, even though the eccentricity is low. But the conditions in the two hemispheres are so different as regards the distribution of land and water that it is not safe to rely on this argument.

The next sub-section, on " the causes of ocean currents ", seems to the reviewer obscure. The gravity circulation and such important factors as temperature and evaporation are scarcely touched upon.

If the discussion of the causes of ocean currents is obscure, that of " Action and Reaction of Physical Agents ", which deals with the processes of radiation in the atmosphere, is still more so. The author goes, apparently, for his information about radiation to Tyndall and Croll. Modern work, particularly the important researches of Angstrom, Abbot, Aldridge, and Simpson, are not mentioned. Our knowledge of radiative processes and the absorption, emission, and reflection of radiation of various wave-lengths by the sea, land surfaces of various kinds, snow and ice, cloud, water vapour, and the permanent gases of the atmosphere is far more precise than it was in Croll's day.

Halligan says that " A good many of the writers on ice age matters seem to be confirmed in the idea that the quantity of snow and ice melted must be proportional to the amount of sun-heat received, but this assumption is totally opposed to the known facts. We know that there is no place on the face of the globe where the amount of heat received from the sun is not far more than sufficient to melt all the snow which falls upon it, so that if it were true that the amount of snow melted is proportional to the amount of heat received by the snow, then there could be no such thing as perpetual snow ". This statement is very difficult to understand. In the first place, the air over polar ice sheets is continually being renewed, air which has lain over it for some time being replaced by warmer air from lower latitudes. The amount of heat lost from the ice surface by radiation will depend on the temperature of the air above it. So, also, will the amount gained or lost by conduction. The higher the temperature of the air, the less will be the net loss by either process. The average temperature of the air will certainly be greater, generally speaking, the more intense the sun's radiation. Next, though a portion of the solar radiation is intercepted by the atmosphere, and a still greater portion reflected from a snow surface, a fraction of it is absorbed by the snow. If the intensity of the radiation increases, more heat will be absorbed. Thus, even if the temperature of the snow never rises to freezing point, its cooling power will be reduced by an increase in the incoming radiation. If the temperature does rise to freezing point, ice will be melted, and the more the radiation received, the more will be the ice melted. Some of the resulting water will run away and not be re-frozen. In any case, at the edge of an ice sheet there is opposition of melting and freezing processes, and, if things have had time to settle down to a steady state, clearly the ice sheet will tend to expand or contract according as the amount of solar radiation decreases or increases. Indeed, there would seem to be a good deal of truth in the statement that the amount of snow and ice melted must be proportional to the amount of sun-heat received.

The following section, headed "Fundamental Oceanographical Facts" gives a quotation from "Thalassa" by J. J. Wild which is intended to give a summing up of our knowledge of the circulation of oceanic water. Mr. Halligan refers to it as a "masterly epitome". It does mention the factors of temperature, evaporation, and salinity, but, in its present context at any rate, and with no explanatory diagram, the reviewer finds it extremely confusing. Halligan then adopts Croll's main argument that changes of eccentricity would bring about changes of climate by diverting currents of warm ocean water from one hemisphere to the other. In the section on "Fundamental Meteorological Facts" it is expressly stated that "when the eccentricity of the earth's orbit is at a high value, and the northern winter solstice is in perihelion, it necessarily follows that the medial line of the trade winds is shifted to the north, and consequently the south-east trade winds are stronger than the north-east, and blow over upon the northern hemisphere, as far probably as the Tropic of Cancer". Again there is no proof. If the south-east trade winds were to push far across the equator, they would not retain their south-easterly direction but turn to the south-west as does the summer monsoon in India. However, Halligan continues, "the result is that all the great equatorial currents of the ocean are impelled into the northern hemisphere, which thus, in consequence of the immense accumulation of warm water, has its temperature raised and snow and ice to a great extent must then disappear from the Arctic regions. When the precession of the equinoxes brings round the winter solstice to aphelion the condition of things in the two hemispheres is reversed, and the north-east trades then blow over upon the southern hemisphere, carrying the great equatorial currents with them. The warm water being thus withdrawn from the northern hemisphere, its temperature sinks enormously, and snow and ice begin to accumulate in temperate regions. The amount of precipitation in the form of snow in temperate regions is at the same time much increased by the excess of evaporation in low latitudes, resulting from the nearness of the sun in perihelion during summer."

These arguments are based principally on Croll's interpretation of the Gulf Stream and his calculations with regard to it. A portion of the Gulf Stream comes from the southern hemisphere, but it has to be remembered that the shape of the continent of South America has much to do with this. Croll's computation of the heat carried by the Gulf Stream will be discussed later.

But it is in reference to the " Atmospheric Circulation " that Halligan, as did Croll, makes his most fundamental mistake, one which has affected all his other reasoning. He states that "*no heat can be transported to temperate or polar regions by winds*" (the italics are his). It is extraordinary that a view so obviously contrary to our everyday experience should be seriously maintained. Surely, in Australia northerly winds bring warm weather and southerlies cold, and northerlies transport heat from tropical to temperate latitudes! The line of reasoning is that the surface winds in all latitudes blow with a component towards the equator and consequently are transporters of cold only, while the return currents are located at levels where temperatures are low and they cannot, therefore, be carrying heat poleward. In the first place, however, in no zone of the earth do the surface air currents constantly have an equatorward component. Even in the trade wind zone the direction is by no means constant, a considerable proportion of the winds having a poleward component, while in the zone of westerly winds, the net surface flow is almost certainly polewards. Again, if the atmosphere over the polar regions is cooled by the ice and snow surface, as Croll and Halligan are apparently prepared to agree, whence does it get its heat? The fundamental error, however, is in assuming that temperature alone is a measure of the heat content of a mass of air. To know the latter we must know, also, the pressure. The normal average condition over the earth is for the cold air at a high level to have a greater heat content than the warmer air at the surface. If brought to the surface it will be warmer than the surface air. Only in very exceptional circumstances can it have an appreciably lower heat content than the surface air. In other words, the lapse rate of temperature in the atmosphere is normally less than the adiabatic rate, or, the air at the higher levels is *potentially* warmer than the surface air. Halligan's own account of the effect of Fôhn winds in Siberia should have sufficed to put him on his guard against the fallacy of this, his principal argument. Again Croll, while admitting that south-easterly winds bring warmth to England, claims that they are originally cold winds which have descended from the cold upper strata of the atmosphere, and that the warmth they bear has been imparted to them by the ocean. Even so, they would of course be transporting heat polewards. But actually their temperature would rise as they descended owing to the increase of pressure and they would reach the surface as warm winds. Currents in the upper air, though their temperatures be low, transport enormous quantities of heat poleward.

However, Halligan follows Croll in believing that " the ocean currents were the transporters of heat from the tropics to the polar regions, and also the transporters of cold from the polar regions to the tropics ". Ocean currents are, of course, transporters of heat, but not nearly so important as air currents.

A section of the paper is devoted to " Theories and Hypotheses on the Causes of Glacial Epochs ", various theories being reviewed critically. In the course of this it is stated that " a general diminution of heat can never produce a glacial epoch ". This question has been very thoroughly and logically discussed by Sir George Simpson, and a careful reading of his papers should have enabled Mr. Halligan to avoid the pitfalls he has encountered. Sir George cannot produce direct evidences of large variations in solar radiation, but few people would deny that with sufficient variation it would be possible to account for either glacial or inter-glacial periods.

Generally, this section and the next on " Are Glacial Epochs Synchronous in Both Hemispheres, or Alternate ? " are permeated with the same fallacious arguments as the earlier ones.

There follows a section on Croll's Theory and another devoted to the championing of it against various critics. In the course of these it is stated that "Croll's theory is not an astronomical theory". The prime causes of climatic changes, according to Croll, namely precession and the variation of the eccentricity of the earth's orbit, are astronomical. Since climate is an assemblage of physical phenomena, naturally any changes in it must be exhibited through physical processes, whatever the nature of the causes. Therefore, it is difficult to understand the abovementioned objection. Croll's theory demands that glacial epochs should not be synchronous in both hemispheres, but the weight of the geological evidence in the case of the Pleistocene glaciation does not support this view.

Now, the principal evidence advanced by Croll in favour of his theory is based on his calculation of the amount of heat transported from the equatorial regions by the Gulf Stream, and it is, therefore, proposed to discuss this in some detail. Croll calculates that the Gulf Stream where it emerges from the Straits of Florida is equivalent to a stream 50 miles wide and 1,000 feet deep, flowing at the rate of four miles an hour. In order to be conservative however, he bases his further computations on a speed of two miles an hour. He assumes an average temperature on leaving the Straits of 65°. He estimates that the stream before it returns from its northern journey is on the average cooled down to at least 40°, "consequently it loses 25° of heat". He, therefore, concludes that the stream carries, approximately, $77 \cdot 5 \times 10^{18}$ foot-pounds of heat energy from the tropics per day. He assumes this all to be delivered to the temperate and polar regions. The amount thus conveyed, he says, is equal to all the heat which falls upon the globe within 32 miles on each side of the equator, that is, on a zone about one degree wide. Since the width of the Atlantic is only about one-sixth of the circumference of the globe, this would mean that the Gulf Stream conveys from the tropical Atlantic as much heat as falls on a band 6° wide. If a velocity of four miles a day were taken instead of two, the band would become 12° wide, equivalent to about half the area of the Atlantic between the latitude of Florida Strait and the equator. The mere statement of the result in this way is sufficient, in the reviewer's opinion, to show that it is impossible. But of the radiation from the sun approximately 40 per cent. is reflected back unchanged, while Simpson has shown that another 50 per cent., about, is radiated back to the sky from the tropics. This only leaves something of the order of 10 per cent. to be transported to higher latitudes. As regards Croll's computation, even if it is true that on the average the waters of the Gulf Stream are cooled from 65° to 40°, it does not follow that the return currents at the latitude of the Florida Straits have a temperature of 40°. To calculate the flow of heat it would be necessary to know the temperature and movements across the whole cross-section of the Atlantic at various latitudes. Again, Croll neglects the heat lost from the Gulf Stream by radiation to space, which, owing to its slow movement, must be a large fraction of the total excess heat carried. Nor is the effect of winds at all adequately discussed.

It is possible to point to many other inaccuracies in Croll's work. Thus, he appears to consider that radiation from a black body is probably proportional to its absolute temperature, whereas we know that it is proportional to the fourth power of it. He does not believe that the gravity circulation of the ocean is important, stating on p. 101 of the 1890 edition of "Climate and Time" that "If ocean currents result from difference of specific gravity between waters in tropical and polar regions, as Maury maintains, then it is necessary to assume that they are descending currents. Whatever be the cause which may give rise to a difference of specific gravity, the motion which results from the difference is due wholly to the force of gravity; but gravity can produce no motion unless the water descend." Gravity would certainly tend to lower the mean level of the mass of water concerned, but, while the more dense elements would tend to move downwards, the less dense would, on the whole, rise. Any simple circulation is much modified, of course, by the deflecting force due to the earth's rotation. It is now well known that gravity is the principal cause of ocean currents.

On p. 28 of the same edition Croll says in reference to air currents, "The only currents which flow from the equatorial regions are the upper currents, or anti-trades as they are called", and "the upper currents of the trade-winds, even at the equator, are nowhere below the snow-line." Neither of these statements is true, even if we disregard the great monsoon currents which flow outwards from the equatorial regions, such as the south-west monsoon of India.

If Croll's explanation of the processes by which the ice sheets of a glacial epoch are produced were correct it is difficult to see how the process could ever be reversed and the ice melted.

REFERENCES.

Below are listed a few works which, together with the references given in them, give authoritative accounts of the present status of our knowledge of the various aspects of the problem we have been discussing.

C. L. Pekeris: "The Development and Present Status of the Theory of the Heat Balance in the Atmosphere", *Massachusetts Institute of Technology*, Meteorological Course, Professional Notes No. 5, 1932.

C. G. Rossby and R. B. Montgomery: "On the Momentum Transfer At the Sea Surface", *Massachusetts Institute of Technology and Woods Hole Oceanographic Institution*, papers on Physical Oceanography, 1936, *4*, No. 3.

W. J. Sandström: "The Hydrodynamics of Canadian Atlantic Waters", *Canadian Fisheries Expedition*, 1914-15.

G. C. Simpson: "World Climate During the Quaternary Period", *Q.J.R. Meteor. Soc.*, 1934, *60*, 425.

G. Schott: (1) "Geographie des Indischen und Stillen Ozeans"; (2) "Geographie des Atlantischen Ozeans", Verlag von C. Boysen, Hamburg, 1935.

NOTE BY MR. G. H. HALLIGAN.

On p. 230, line 14 of my paper, after the words "a very great extent", the following words should be inserted: "But if the winter under these circumstances should happen when the earth is in the perihelion of its orbit the earth would be 14,212,700 miles nearer the sun in winter than in summer".

This short sentence was omitted by my typist, and for this I apologise, and I would beg to thank Dr. Kidson for calling attention to it.

BÆCKEOL.

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and J. L. SIMONSEN, D.Sc., F.R.S.,
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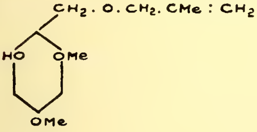
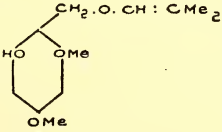
(*Manuscript received, September 29, 1937. Read, November 3, 1937.*)

Some years ago (Penfold and Morrison, *J. Proc. Roy. Soc., N.S.W.*, 1922, *56*, 87) the essential oils from various species of *Myrtaceæ*, more especially *Bæckea crenulata* and *Darwinia grandiflora*, were shown to contain a phenol, $C_{13}H_{18}O_4$, crystallising in yellow prisms, m.p. 103–104°. This phenol, for which we propose the name Bæckeol, has now been prepared in sufficient quantity for the determination with some degree of certainty of its constitution.

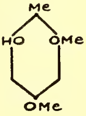
Bæckeol contains two methoxy groups and one hydroxy group, giving a *monoacetyl* derivative, m.p. 71–72°; its alcoholic solution gives with ferric chloride a bluish black coloration. We suggest that the phenol is most probably represented by (1) or (1a), since on fusion with sodium ethoxide at 200° it gives phloroglucinol α-methyl ether (II), m.p. 67–68° (compare Curd and Robertson, *Journ. Chem. Soc.*, 1933, 441), and *iso*butyric acid on oxidation with hydrogen peroxide in alkaline solution.



(I)

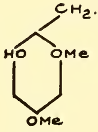


(Ia)

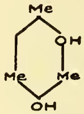


(II)

Whilst the formation of the phloroglucinol derivative establishes beyond question the positions of the substituents in the aromatic nucleus, the actual structure of the side chain was not rigidly proved. Attempts to confirm this structure by ozonolysis were unsuccessful, since, although formaldehyde was obtained in traces (dimedone test), the main products of the oxidation could not be identified. Support for the representation (I) was, however, obtained by the oxidation of bæckeol methyl ether with hot potassium permanganate in alkaline solution. Although the main product of the oxidation was a gummy acid, which could not be purified, a small quantity of a neutral *substance*, was isolated which crystallised in thin prisms, m.p. 65–66°, and had the composition $C_{13}H_{18}O_5$. It reacted readily with 2 : 4-dinitrophenyl-hydrazine to give an amorphous hydrazone, and we suggest that it is probably the ketone (III) formed by the normal oxidation of the methylene group in (I). Unfortunately the quantity of material available was insufficient for further investigation.



(III)

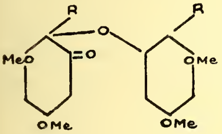


(IV)

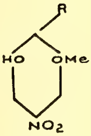
Prior to investigating the action of sodium ethoxide on the phenol it was heated with sodium methoxide at 250°, when removal of the side chain was accompanied by reduction, a phenol, $C_9H_{12}O_2$, m.p. 150–151°, being obtained. There can be little doubt that this phenol, which did not contain a methoxyl group, is mesorcin (IV). The reducing properties of sodium methoxide are of course well known, whilst the mobility of *O*- and *C*-methyl groups in the phloroglucinol nucleus has been observed previously (compare *inter al.*, Boehm, *Annalen*, 1903, *329*, 321; Hems and Todd, *Journ. Chem. Soc.*, 1937, 562), hence the formation of mesorcin is of no value in the determination of the structure of bæckeol.

The facility with which bæckeol can be reduced was further exemplified by its behaviour on catalytic hydrogenation. By the courtesy of Professor I. M. Heilbron, F.R.S., of the University of Manchester, Dr. H. Jackson carried out a microhydrogenation in the apparatus described by Jackson and Jones (*Journ. Chem. Soc.*, 1936, 895). On the basis of the formula, $C_{13}H_{18}O_4$, the hydrogen absorption corresponded to six double bonds in the cold and 6·7 on heating. Whilst the aromatic nucleus and the ethylenic linkage in the side chain would account for four double bonds, the additional three can be explained only if we assume that the hydroxyl group and two of the three ether oxygens were also reduced.

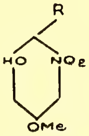
Like methylnaphthol (Pummerer and Cherbuliez, *Ber.*, 1914, *47*, 2957), bæckeol is readily oxidised by potassium ferricyanide in alkaline solution, giving an *oxide*, $C_{26}H_{34}O_8$, m.p. 127–128°, for which on the basis of the experiments of Pummerer and his collaborators (*Ber.*, 1919, *52*, 1392, 1403) we suggest the structure (V).



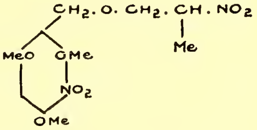
(V)



(VI)



(VII)



(VIII)

[R= $-CH_2.O.CH_2.CMe:CH_2$]

On nitration bæckeol yields a *nitro*-derivative, $C_{11}H_{12}O_5(OMe)$, m.p. 106°, which is probably represented by either (VI) or (VII), a methoxyl group having been replaced by the nitro group. This nitro-phenol, which gives with alcoholic ferric chloride a red coloration, is somewhat remarkable in that it dissolves in alkali to give a colourless solution. Bæckeol methyl ether gives on nitration a *dinitro-derivative*, $C_{13}H_{18}O_8N_2$, m.p. 115–116°, for which we suggest the representation (VIII).

Whilst we regard these experiments as affording strong evidence for the structure (I) assigned to bæckeol, it is proposed to attempt the synthesis of the phenol.

EXPERIMENTAL.

Bæckeol crystallised from methyl alcohol in faintly yellow prisms, m.p. 103–104°, the colour persisting after sublimation in a low vacuum (found: C, 65·3; H, 7·7; $C_{13}H_{18}O_4$ requires C, 65·5; H, 7·5%). The phenol showed very weak acidic properties, being soluble in hot alkali but only very sparingly so in cold. It was not reduced by zinc dust in alkaline solution; on digestion with mineral acids (hydrobromic or hydriodic acids) it gave deep red amorphous products. In acetic acid solution it readily absorbed bromine and a crystalline solid separated, which rapidly decomposed with evolution of hydrogen bromide.

The *acetate*, prepared by digesting the phenol with acetic anhydride, crystallised from dilute methyl alcohol in well formed colourless prisms, m.p. 71–72° (found: C, 64·0; H, 7·0; $C_{15}H_{20}O_5$ requires C, 64·3; H, 7·1%).

Nitration of Bæckeol.

The phenol (0·1 g.) was dissolved in a nitrating mixture (nitric acid (*d* 1·4), 1 c.c.; sulphuric acid, 1 c.c.) and kept at room temperature for two hours. The reddish brown solution was poured on to ice and the gum, which separated, was triturated with sodium carbonate solution, which left undissolved a little unchanged phenol. Acidification of the sodium carbonate solution deposited the *nitro-phenol* (0·2 g.), which crystallised from methyl alcohol in long prisms, m.p. 106° (found: C, 53·7; H, 5·6; N, 4·7; OMe, 11·2; $C_{11}H_{12}O_5N(OMe)$ requires C, 53·5; H, 5·6; N, 5·2; OMe, 11·4).

Oxidation of Bæckeol.

(*a*) *With Potassium Ferricyanide.* To a boiling solution of the phenol (0·2 g.) in dilute potassium hydroxide solution (KOH, 0·5 g.; H_2O, 5 c.c.) a solution of potassium ferricyanide (ferricyanide, 3·3 g.; H_2O, 25 c.c.) was added gradually, the boiling being continued for eight hours. The *oxide*, which separated from the cooled solution, crystallised from much hot water in colourless needles. These contained apparently solvent of crystallisation and when air dried had m.p. 97°, resolidifying and then melting at 127°. After drying in a vacuum over phosphorus pentoxide the oxide had m.p. 127–128° (found: C, 66·0; H, 6·9; $C_{26}H_{34}O_8$ requires C, 65·8; H, 7·2%).

(*b*) *With Hydrogen Peroxide.* To a solution of the phenol (0·4 g.) in methyl alcoholic potassium hydroxide solution (KOH, 0·4 g.; methyl alcohol, 4 c.c.) cooled in ice, hydrogen peroxide (100 vol., 0·8 c.c.) was added. After keeping in ice for 30 minutes the mixture was allowed to attain room temperature, when it became red in colour and some heat was generated. After remaining overnight a further quantity (0·8 c.c.) of hydrogen peroxide was added and the solution heated under reflux for two hours. Addition of water and removal of the alkali with carbon dioxide precipitated unchanged phenol (0·1 g.). The filtrate was evaporated on the water bath until free from alcohol, acidified with sulphuric acid and distilled in steam. The distillate was neutralised with standard alkali, and after the addition of the corresponding quantity of *p*-bromophenacyl bromide (in alcohol) warmed on the water bath for one hour. The crystalline *p*-bromophenacyl ester so obtained had m.p. 74–76° and in admixture with an authentic specimen of the *p*-bromophenacyl ester of *iso*butyric acid, m.p. 75–76° (found : Br, 28·4 ; $C_{12}H_{13}O_2Br$ requires Br, 27·9%).

Action of Sodium Methoxide on Bæckeol.

A mixture of the phenol (0·5 g.) and sodium methoxide (Na, 0·5 g. ; methyl alcohol, 8 c.c.) was heated in a sealed tube at 250° for eight hours in an atmosphere of nitrogen. After the addition of water the solution was acidified and repeatedly extracted with ether. The ethereal extract was washed with sodium carbonate solution, dried and evaporated, when an oil (0·3 g.) remained, which partially crystallised. After trituration with ligroin (b.p. 40–60°) the solid, m.p. 148°, was recrystallised from *cyclo*hexane and then twice from water from which it separated in long felted needles, m.p. 150–151° (found : C, 71·0 ; H, 7·5 ; OMe, 0 ; $C_9H_{12}O_2$ requries C, 71·1 ; H, 7·9%). The phenol gave with ferric chloride a transient green coloration and it reduced immediately an ammoniacal solution of silver nitrate. As mentioned on p. 292, there can be little doubt that this substance is mesorcin.

Action of Sodium Ethoxide on Bæckeol.

A mixture of bæckeol (0·5 g.) and sodium ethoxide (Na, 0·5 g. ; ethyl alcohol, 10 c.c.) was heated in a sealed tube at 200–220° in an atmosphere of nitrogen for four hours. After the addition of water the alcohol was removed on the water bath, the cooled solution acidified and extracted with ether. Evaporation of the dried extract left an oil which crystallised on keeping, becoming red on exposure to the air. Purification was best effected by sublimation at 150° in a low vacuum, which removed a coloured impurity and the phenol then crystallised from ligroin (b.p. 60–80°) in long fine needles, m.p. 67–68°, both alone and in admixture with an authentic specimen of methylphloroglucinol α-methyl ether kindly given us by Professor A. Robertson. The phenol gave no colour with alcoholic ferric chloride. (Found : C, 64·3 ; H, 7·2 ; OMe, 36·7, 36·5 ; $C_7H_6O(OMe)_2$ requires C, 64·3 ; H, 7·1 ; OMe, 36·9%).

Nitration of Bæckeol Methyl Ether.

The methyl ether was obtained as an oil when the potassium salt of bæckeol was repeatedly treated with a large excess of dimethyl sulphate. It gave no colour with alcoholic ferric chloride. Bæckeol was not attacked by an ethereal solution of diazomethane. For nitration, the methyl ether (0·2 g.) was mixed with nitric acid (*d* 1·4; 2 c.c.), the ether dissolving to a yellow solution with generation of some heat. After keeping for fifteen minutes gentle warming caused a vigorous reaction, the mixture was cooled, addition of ice precipitating a gum. This was dissolved in ether, the ethereal solution washed with sodium carbonate solution, dried and evaporated. The residue (0·1 g.) crystallised from dilute methyl alcohol in colourless prisms, m.p. 115–116° (found: C, 47·6; H, 5·2; N, 8·2; $C_{13}H_{38}O_8N_2$ requires C, 47·3; H, 5·4; N, 8·5%). The *dinitro-ether* dissolved in sulphuric acid to give a yellow solution. If bæckeol methyl ether is digested with dilute nitric acid it is oxidised to oxalic acid.

Oxidation of Bæckeol Methyl Ether with Potassium Permanganate.

To a well stirred suspension of the methyl ether (2 g.) in hot potassium hydroxide solution (300 c.c.; KOH, 2 g.) finely divided potassium permanganate (40 g.) was added gradually. After the oxidation was complete the filtered solution was concentrated, acidified, and extracted with ether. Evaporation of the solvent left a gum (0·5 g.), which was stirred with sodium carbonate solution, when a solid (0·03 g.) remained undissolved. The *substance* crystallised from ether-ligroin in thin prisms, m.p. 65–66° (found: C, 61·9; H, 7·3; $C_{13}H_{18}O_5$ requires C, 61·4; H, 7·1%). Acidification of the sodium carbonate solution gave a gum which could not be crystallised. It dissolved in nitric acid to give an intense emerald green solution, becoming somewhat bluish on keeping and reddish brown on dilution with water. On solution in sulphuric acid it gave a yellow colour, which when shaken with benzene became green. Oxidation of the acid with dilute nitric acid gave oxalic acid.

ACKNOWLEDGMENTS.

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STRATIGRAPHY AND PHYSIOGRAPHY OF THE GOULBURN RIVER DISTRICT, N.S.W.

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(With three text-figures.)

Communicated by Dr. W. R. Browne.

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Contents.

Introduction.

The Goulburn River District lies immediately to the south of the Liverpool Range and extends west from the Hunter River Valley as far as the Main Dividing Range between Mudgee and Cassilis. As a result of reconnaissance work in this district a considerable area of Jurassic strata has been recognised overlying the north-western extremity of the Upper Coal Measures and Triassic Sandstone. A detailed study of the stratigraphy in the area bounded by the Cassilis-Merriwa road on the north and the village of Wollar to the south, has shown the area to be of considerable importance in regard to the relation between Triassic and Jurassic strata in north-western New South Wales.

The physiography of the area is important in its relation to the differential uplifting of eastern New South Wales during the Tertiary era. The structure of the area is discussed in the present paper with respect to the age of folding and the possible influence of the structures upon the development of the present topography. The physiography has been included with the general geology as the two are so intimately connected.

STRATIGRAPHY AND REGIONAL GEOLOGY.

Kamilaroi.

In the vicinity of Wollar the surface formation is Triassic sandstone with Upper Coal Measure strata outcropping in the valleys which carry the headwaters of the Goulburn River. The general dip of the strata in this part of the area is N. 20° E., at 1·5°.

There is no outcrop of Upper Marine strata in the area, although some 500 feet of coal measure beds are exposed in the deeper dissections to the east of Wollar. The Coal Measure sediments consist of typical Upper Kamilaroi shales with soft sandstone bands, of which several are tuffaceous, and coal-bearing horizons with which oil shales are associated.(1)

Triassic.

Wollar Sandstone. This formation consists of Triassic sandstone with a maximum thickness of about 650 feet. It is actually a coarse white sandstone crowded with small white pebbles, so that it may almost be described as a fine conglomerate, and it is notably more conglomeratic towards the base. The beds are perfectly conformable with the underlying coal measures, but are separated from them by a well-defined junction, not an indefinite passage such as occurs in parts of the Hunter Valley between the Triassic and Kamilaroi. In the vicinity of Wollar the base of the Triassic is marked by a bed of soft white sandstone containing fragments of green shale.

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(1) L. J. Jones: *Ann. Rept. Dept. of Mines*, 1925, p. 129.

The Wollar Sandstone exhibits an eroded peneplain surface, and passing to the north it increases in thickness and eventually dips below a younger series of shales which are followed in turn by a sandstone formation. These superimposed sediments are conformable with the Wollar Sandstone and provide the surface for an extension of the peneplain as far north as the foothills of the Liverpool Range.

Comiala Series. The shales occurring on top of the Wollar Sandstone have been given this name for field purposes. The series as a whole has proved poor in plant remains, and as yet has not yielded any fossils of value in allotting a definite age to the beds. The shales form small outliers to the north of Wollar and commence to occupy a continuous horizon along a line joining Merriwa and the Talbragar Fish Beds, constituting an outcrop for about 50 miles across the area, and exhibiting a maximum thickness of 210 feet at a position north-north-east from Wollar.

The Comiala Series is composed mainly of fine-grained clay-shales, light grey to blue in colour, and dark blue to black mudstones with a hackly fracture. Tuffaceous shales are common, passing into impure tuffs in many cases. Several hard fine sandstone bands occur in the series, especially towards the upper and lower limits of the shales, where passage beds mark transitions into both overlying and underlying sandstones. There is also a tendency towards the development of several thin coal seams, where carbonaceous shales pass into impure coal usually no more than a few inches in thickness ; in one case a two-inch band of bright cannel coal has developed.

Jurassic.

Munmurra Beds. These overlie the Comiala Series and consist mainly of soft red to yellow sandstone of a coarse and porous nature. Immediately above the transitional beds from the underlying shales, there occurs a conglomerate horizon, from three to ten feet in thickness, carrying boulders of slate, schist, and quartz-porphyry up to twelve inches in diameter. Many of the slate and schist boulders consist of a material very similar in general texture to that which occurs in the Silurian and Devonian formations between Ulan and Mudgee.

Other than this one conglomerate horizon the formation is fairly homogeneous, and, although much of the surface has been removed by erosion, a thickness of at least 300 feet is indicated at the margin of the Liverpool Range basalt, where the general dip of the sandstone is almost due north at about 1·5°. The Munmurra Beds have been traced from the Merriwa River at Merriwa to the Talbragar River between Uarbry and the Talbragar Fish Beds. The relation of the various beds is illustrated in Text-fig. 1, and their general distribution throughout the area in the accompanying map (Fig. 2).

Tertiary.

Alkaline Intrusives. To the south of the Goulburn River there occur several small alkaline intrusive masses of Tertiary age. The most important of these are the Barigan laccoliths, which consist mainly of nepheline-tinguaite and occur some 15 miles to the south of Wollar, where the Wollar Creek heads in the Main Dividing Range.⁽²⁾ A large mass of alkaline igneous rock occurs in the Wollar Valley, one mile to the south of Wollar. The material may best be described as a sodalite or analcite-tinguaite. It forms a flat tabular body and has a dip of about 2° in a direction approximately N. 20° W., which is conformable with the dip of the surrounding coal measure strata. The mass is about half a mile in width and some 170 feet in thickness, and, although no sediments have been found on top of the igneous rock, the underlying coal measure shales are hardened, and there is little doubt that it represents a sill or laccolith intrusive into the Upper Coal Measures. The material of the sill is very similar to a tinguaite which occurs as an intrusive mass at Kerribee Pass, on the main road between Bylong and Denman.

Olivine Basalts. The north-eastern side of the area is entirely occupied by the Tertiary olivine basalts of the Liverpool Range, rising some 1,500 feet above the sandstone peneplain surface. The basalt forms thick flows, which have covered the country to the south of the Range. Tertiary volcanic necks are common along the southern margin of the main flows, and consist of olivine-dolerite with volcanic breccia in a few cases.

Correlations.

The soft red and yellow sandstone of the Munmurra Beds overlying the Comiala Series is of Jurassic age, as it

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⁽²⁾ *Mem. Geol. Sur. N.S.W.*, Geology No. 3, 1906, p. 236.

occupies an horizon equivalent to that of the Jurassic Mumbedah sandstone, described by Mr. E. J. Kenny,(3) between Dunedoo and Binnaway, with which it is lithologically identical. It also contains fossil fish of Lower Jurassic age in the Talbragar Fish Beds, just west of the Main Divide. Professor David placed the Talbragar Fish Beds as equivalent to the Middle Lias of Europe and the base of the upper part of the Lower Clarence Series of New South Wales.(4) The Fish Beds form an integral part of the sandstone series overlying the Comiala shales and occur towards the base of the sandstone, which may be regarded as equivalent to the upper part of the Lower Clarence Series, or to the Middle Clarence Series.

The occurrence of Jurassic sandstone on the southern side of the Liverpool Range suggests an unbroken extension of the greater Jurassic formation lying to the north and north-west of the Range, and the Munmurra Beds probably form the actual southern margin of the intake beds of the Great Artesian Basin. In connection with this suggestion it is significant that the line of outcrop of the Comiala shales, separating the Jurassic and Triassic sandstones, forms the southern limit to sub-artesian bores. In the country to the north of this line sub-artesian water may be obtained at depths varying from 200 to 500 feet.

There is not yet sufficient palæontological evidence to give the exact age of the Comiala Series. On considering their lithological resemblances and stratigraphical position, it is evident that there is a possibility of their being either Upper Triassic and equivalent to the Wianamatta Series, or Lower Jurassic and equivalent to the Lower Lias. The conglomerate horizon at the base of the overlying Jurassic sandstone suggests a break in sedimentation, favouring a Triassic age for the shales, but at several places the conglomerate cuts out completely, its place being taken by passage beds from the underlying shales, and the transition is similar to the passage from the Triassic sandstone at the base of the shale series.

The Comiala Series exhibits a maximum thickness near the junction of the Krui and Goulburn Rivers, and shows a marked tendency to thin towards the east, south, and west, which suggests a lake-deposit formed on the surface of the Triassic sediments. This also favours a Triassic age,

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(3) *Ann. Rept. Dept. of Mines, N.S.W.*, 1925, p. 137.

(4) Explanatory Notes to New Geological Map, 1932.

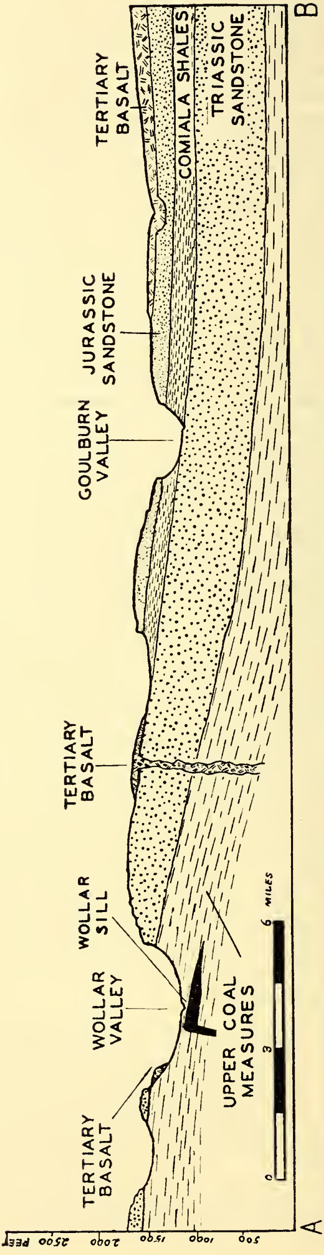

Fig. 1.—Sketch Section (along A–B, Fig. 2) across the Upper Goulburn River District.

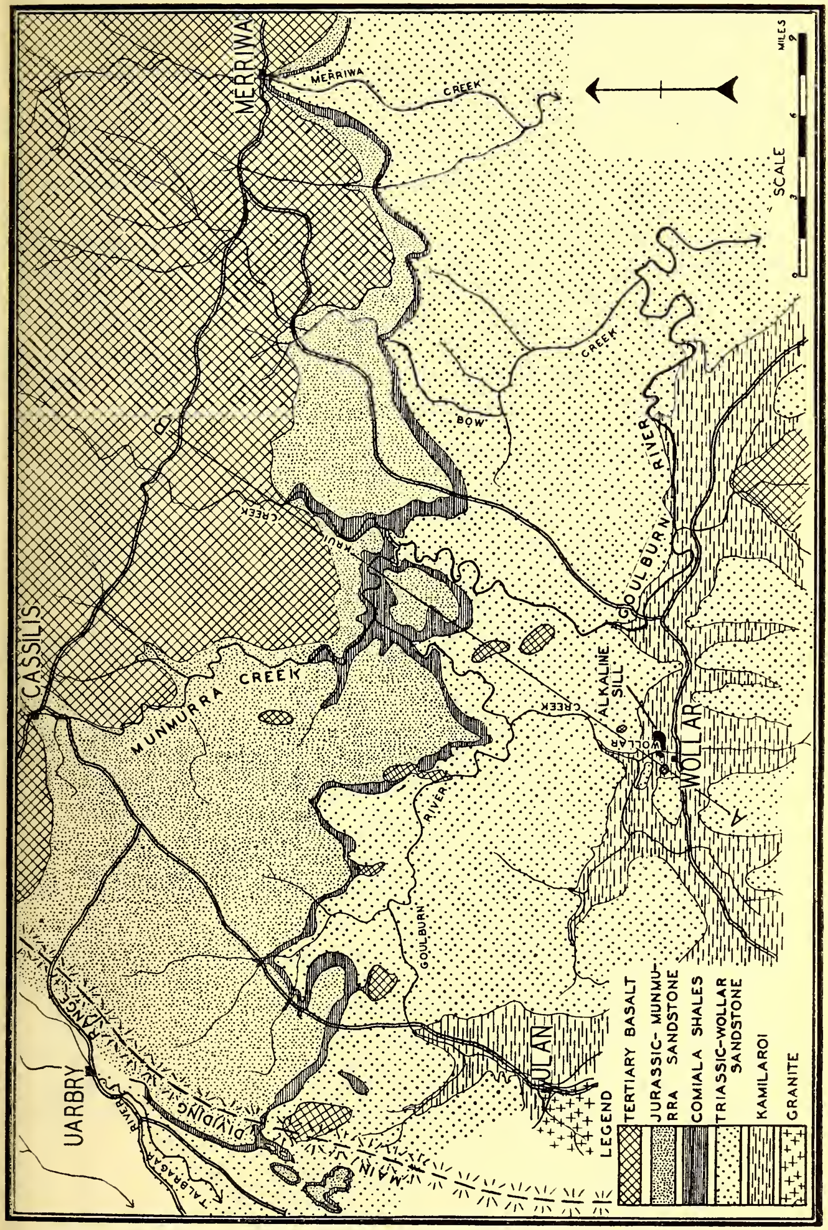

Fig. 2.—Geological sketch map of the Upper Goulburn River District.

equivalent to the Wianamatta Series, but is not conclusive, as the shales exhibit in places a gradual transition into the overlying Jurassic sandstones. Although their age is still uncertain, the Comiala shales represent an important stratigraphical unit, as the horizon may be taken as a definite line of demarcation between Triassic and Jurassic sediments, and should provide a useful indicator horizon for such a distinction if followed into the Mesozoic sediments to the west of Uarbry.

From a study of the lithology and stratigraphical sequence in the Mesozoic strata of the Goulburn River district, a tentative correlation has been made with the Mesozoic sediments of the Dunedoo-Binnaway area, which were described by Mr. E. J. Kenny and correlated with the Mesozoic strata of the Dubbo-Cobborah and Coonabarabran-Gunnedah districts.(5)

The Munmurra Beds overlying the Comiala Series in the Goulburn River district are considered to be equivalent to the Mumbedah Beds of the Dunedoo-Binnaway area and the Pilliga Beds of the Coonabarabran-Gunnedah district, and it is believed that additional work between Uarbry and Dunedoo will prove them to be continuous with the Mumbedah and Pilliga sandstones.

The correlation of the Comiala shales with the strata of the western districts would seem to depend largely upon the age of the shales. If they are of Lower Jurassic age they could be placed as equivalent to the Upper Merrygoen Beds of the Dunedoo-Binnaway area. The Upper Merrygoen Beds, however, contain " Red Beds " or ironstone bands, which also characterise equivalent strata in the adjoining districts, but such " Red Beds " are rare in the Comiala Series, constituting a feature which does not favour the above correlation. If the Comiala shales are equivalent to the Wianamatta Series of the Triassic System, then they may be correlated with the Napperby Beds of the Coonabarabran-Gunnedah district. This would mean that the Upper Merrygoen Beds and Purlawaugh Series do not extend as far east as the Goulburn River, requiring an overlap by the Mumbedah and Pilliga sandstones, which is made possible by the fact that there is a more definite break in sedimentation at the top of the Comiala Series than at the base.

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(5) *Ann. Rept. Dept. of Mines, N.S.W.*, 1934, p. 86.

The lithology of the Comiala shales would appear to be in favour of the latter correlation, owing to their general similarity to the Napperby Beds as well as their definite resemblance to the Wianamatta Series.

The Wollar Sandstone, separating the Comiala shales from the Permian strata in the Goulburn Valley, is continuous with the Triassic sandstone overlying the Kamilaroi beds to the south-east, and it is expected that eventually it will be shown to be continuous with the Triassic sandstones at Dunedoo, constituting an important link between the extensive Triassic sandstone to the south-east and the more scattered deposits of the western districts.

Geological Structure.

The general dip of the strata on the western side of the area is to the north-east at about 1·5°, while towards the eastern side the direction approaches north, the angle of dip being very low, often less than 1°. At intermediate positions near the middle of the area the dip is about N. 20° E., as illustrated in Fig. 3. This constant change in direction across the area from west to east is undoubtedly due to the position occupied by the Goulburn River district, on the south-western side of a large basin which extends to the north-east.

Although the structure of the area is simple, there are several departures from the almost horizontally-bedded nature of the strata. The most important of these is the Wollar Anticline. Its axis is three miles east from Wollar, running in a direction N. 5° E., and pitching at about 2·5° until it becomes submerged under the Liverpool Range basalt, 16 miles to the north. To the south the fold continues S. 5° W., its crest being almost horizontal. This is the southern development of a small fold affecting both Triassic and Jurassic beds near the junction of the Goulburn and Munmurra Rivers. Here the amplitude is about 50 feet, but it develops as it runs south until it reaches 300 feet in the coal measures to the east of Wollar.

In the Jurassic formation between Wollar and Merriwa there is evidence of a second anticlinal structure running parallel to the fold just described and situated about five miles to the east. This fold appears to have an amplitude of some 200 feet in the northern part of the area, but so far it has not been found in the coal measures to the east of Wollar.

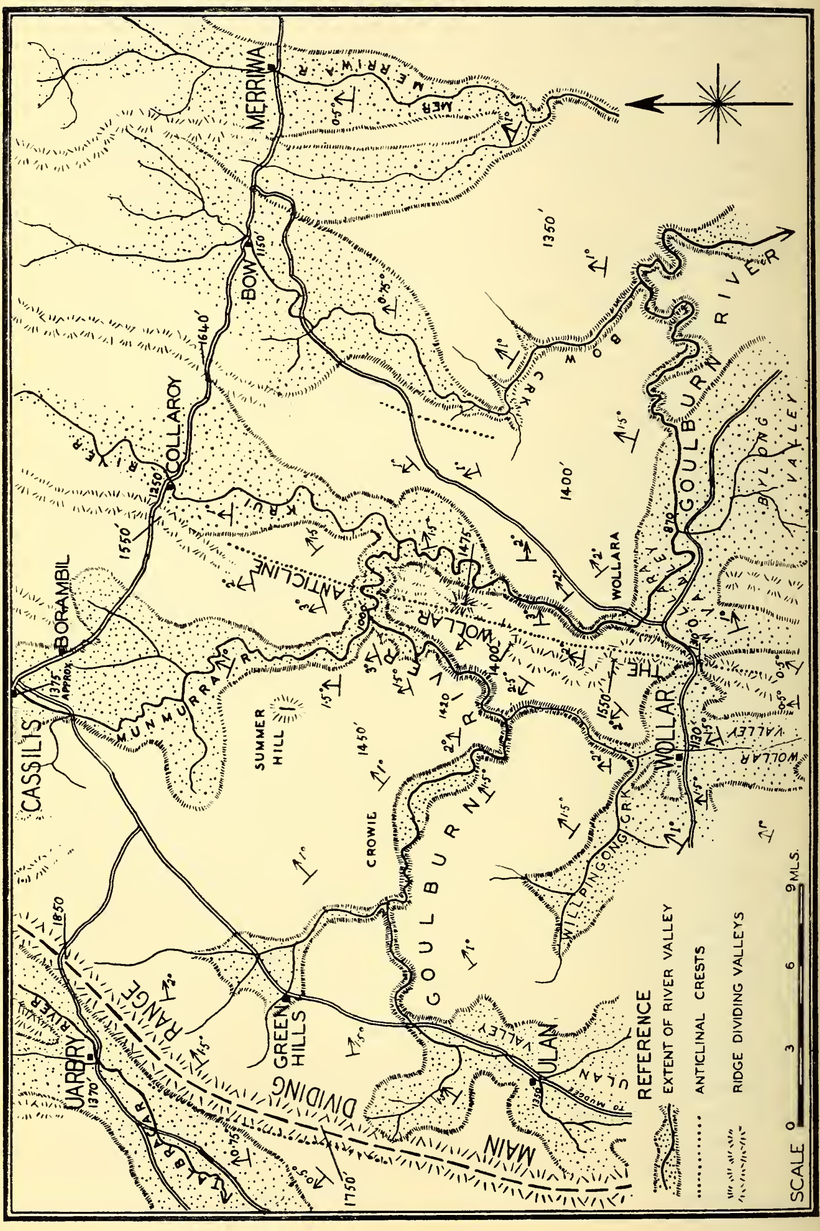

Fig. 3.—Structural and physiographical sketch map of the Upper Goulburn River District.

On the western side of the area, between Ulan and Uarbry, the Main Divide is determined by a low anticlinal fold pitching at about 1° in a direction N. 10° E. The amplitude of this fold has not yet been determined.

In addition to the general north-south folding of the area, the coal measure formations and Triassic sandstone in the vicinity of Wollar and the Bylong Valley suffer a change in dip along a line approximately east and west through Wollar. To the north of this line the average dip is N. 20° E., at about 1·5°, while to the south the strata rise at a very low angle, about 0·5°, the direction of dip becoming N. 30° E. It would appear as though the increase in dip to the north of Wollar is reduced to moderate dimensions on the northern side of the area, but this is somewhat indefinite, as the strata are largely covered by basalt.

The area, although subjected to considerable but gentle folding, seems to be particularly free from any type of faulting on a large scale. It is possible that further work may reveal faults of important dimensions but as yet only minor faults have been measured, with vertical displacements of no more than two or three feet.

PHYSIOGRAPHY.

General Description of the Area.

The late Mesozoic peneplain which dominates the general surface of the country is terminated to the north by the Tertiary basalt of the Liverpool Range, which rises to some 1,500 feet above the old peneplain level. This basalt has been superimposed upon the older surface, which continues to the north under the flows from the Range.

In an east-west direction across the area the peneplain surface rises gradually from an altitude of some 1,100 feet on the western side of the Hunter River Valley to 1,750 feet on the Main Divide in the vicinity of Ulan. The actual Divide is formed at the position where the peneplain level, passing from east to west, ceases to rise and becomes almost horizontal, after which it gradually decreases in height until it eventually falls to the level of the Western Plains, some 1,200 feet in the vicinity of Dunedoo. This gradual rise to a maximum at the Main Divide with the fall to the level of the Western Plains, occupies a distance of about 80 miles, and constitutes a change in elevation of no more than 500 to 600 feet, which occurs uniformly over the distance.

The peneplain surface has been fairly extensively dissected by the Goulburn River and its tributaries, producing a drainage system which consists mainly of wide shallow valleys exhibiting a considerable degree, and in places an advanced stage, of maturity.

From its headwaters in the Main Divide, the Goulburn River runs east to the Hunter River Valley, maintaining a uniform rate of fall at about seven feet to the mile (river miles). The peneplain surface falls to the east at about ten feet to the mile (direct miles). These facts are reflected in a uniform depth of the Goulburn Valley below the peneplain surface, which varies between 300 and 400 feet throughout the entire course of the river.

The Goulburn and its Tributaries.

General. Although the depth of the valley is uniform, the river has excavated several different and rather contrasting valley types, at the same time passing through alternate shale and massive sandstone formations of considerable thickness. At Ulan, three miles from the Main Divide, the river is running in Upper Coal Measure shales with overlying Triassic sandstone. A mature valley two to three miles in width has been developed, with large deposits of alluvium on its floor.

The river runs north-east from Ulan and at the point where it crosses the Mudgee-Cassilis road the base of the Triassic sandstone dips below the river level. It then turns east and immediately enters a narrow sandstone gorge in which floodplains are very limited and in many places completely absent. On reaching the locality of Crowie, about eight miles to the east, the river enters the Comiala shales. At this point the valley widens out and assumes a degree of maturity resembling that of the Ulan Valley. This wide valley continues east from Crowie to the junction of the Goulburn River and the Wollar Creek, on the western side of the Wollar Anticline. From here the river runs north in Wollar sandstone, the valley becoming a narrow gorge 300 feet deep with vertical walls of sandstone. This gorge continues for about five miles and then the river emerges on to the top of the Wollar sandstone, where another wide mature valley has been developed in the overlying Comiala shales, with cliffs of Jurassic sandstone.

This mature section of the valley continues north for three miles and the river then turns east, passing through the Wollar Anticline and continuing for about four miles before it swings back to the south to run along the eastern side of the fold. When the river turns to the south, the north-easterly dip of the strata brings the Triassic sandstone above the river level, and a gorge similar to that on the western side of the fold has been developed in the sandstone. This narrow valley runs south for nine miles until the river passes down stratigraphically into the Upper Coal Measures at Wollara, where a wide mature valley again makes its appearance, and the river turns east.

The northern detour which the river makes into the Jurassic sediments, as described above, constitutes a striking feature, as shown by the accompanying map (Fig. 3). At certain points along the eastern arm of the detour the river is no more than two and a half miles from its course on the western side.

From Wollara the Goulburn River runs east in its mature valley to its junction with the Bylong Valley. Between the Bylong Valley and Sandy Hollow it passes to the north and joins the Merriwa River, where it is again entirely in sandstone strata and where its valley is a gorge; then it runs south-east and the valley opens out to a wide mature type as it returns to the Coal Measure shales near Sandy Hollow. From Sandy Hollow to its junction with the Hunter River near Denman the valley is wide and mature, being carved out of Upper Coal Measure shales.

A typical section across one of the mature sections of the Goulburn Valley would show wide level flood-plains with rather steep concave valley walls, capped with lines of low sandstone cliffs. The river meanders extensively in the flood-plains. The meanders pass diagonally across the valley and at the points where they meet the valley walls the river is engaged in undermining the sandstone cliffs by attacking the softer underlying shales. This constitutes a process of true lateral planation as the river is not lowering its valley floor. At the points where the Bylong, Widdin, and Baerami Creeks join the Goulburn River, extensive mature valleys have been developed in Coal Measure shales. All the southern tributaries of the Goulburn possess wide mature valleys which open out in the deeper exposures of coal measures towards their headwaters, due to the northerly dip of the strata. The northern tributaries, such as the Merriwa and Bow Creeks, enter the Goulburn Valley through narrow gorges, as the sandstone dips below the general creek level on this side of the river.

A feature which characterises the Goulburn Valley below its junction with the Munmurra River is an alternation of sand and black-soil layers in the alluvial flats, which are thirty feet deep in many places. Above its junction with the Munmurra the headwaters of the Goulburn are confined to sandstone and shale formations, while the Munmurra River heads in the basalt of the Liverpool Range, draining the black-soil country to the north of Cassilis. The banded nature of the alluvium below the junction is due to alternate flooding in the two rivers. This process is in operation at the present time, each flood depositing sand or black-soil mud on the low-level flood-plains according to the river responsible for the flooding.

Although the Goulburn River runs entirely in sandstone and shale country, the northern tributaries drain the southern slopes of the Liverpool Range from Cassilis to Bunnan, resulting in extensive black-soil flats between walls of sandstone and shale in the Goulburn Valley, below its junction with the Munmurra River.

In the upper portion of the Goulburn River the deep alluvium in its bed consists entirely of sand, which carries the major portion of the river water below the surface, except under flood conditions. The result is that during the greater part of the year the river exhibits a dry sandy bed at the surface, but water is always flowing through the sand several feet below the surface, and after rain the level of the flowing water slowly rises until it reaches the surface of the sand, the running water gradually appearing further down the river as the sand in the bed becomes saturated.

These minor features, apart from general interest, have a physiographical significance, as they are a function of the stage in base-levelling reached by the Goulburn River. In this connection it is of interest to note that the Talbragar Valley on the western side of the Main Divide is even further advanced in maturity than the Goulburn Valley, although the Main Divide forms the eastern side of its valley in the vicinity of Uarbry, and the top of the Divide is no more than 400 feet above the valley floor.

Tertiary Olivine Basalts. During the volcanic activity of the Tertiary era huge flows of olivine basalt were poured out along a line now represented by the Liverpool Range, flowing down over the country to the south. Subsequent erosion has removed much of the basalt, exposing the underlying sedimentary surface with its original Tertiary topography.

Between Merriwa and Cassilis the streams flowing south to the Goulburn River are now engaged in removing basalt from their Tertiary valleys, the floors and sides of which were covered completely by heavy flows during the outpouring of the basic lavas. In the Munmurra Valley at Cassilis, basalt flows form the valley walls and basalt is *in situ* on the floor of the valley, while one mile further down the same creek sandstone outcrops in the valley floor and forms the western wall to a height of 250 feet above the basalt on the floor at Cassilis. Much the same situation is to be seen where the Merriwa-Cassilis road crosses the Krui Valley, sandstone outcropping on the western side of the valley some 150 feet above the basalt flows which reach the floor of the valley. At Merriwa the basalt is *in situ* on the western side of the valley of Merriwa Creek to within 50 feet of the flood-plain, while on the eastern side sandstone outcrops to a height of 200 feet above the floor of the valley.

There is also evidence of basalt having flowed into the Goulburn Valley. At Crowie, eight miles below the Mudgee-Cassilis road, the valley has been filled completely by a basalt flow from a neck situated three miles away on its northern side. The river has cut a narrow channel through the basalt and is at present running less than 100 feet below the base of the flow in sandstone strata.

At the junction of the Goulburn and Bylong Valleys a large flow of olivine basalt is situated on the floor of the valley, and the river is now running about 200 feet below the level of the basalt, although the valley floor at this point is almost 450 feet below the plateau surface. In the Wollar Valley several flows are situated on the sides of the valley about 250 feet above the present creek level and a similar depth below the plateau surface. At numerous places along the Goulburn Valley residual soil and " grey billy " suggest that basalt existed at one time on the sides of the valley, to within 100 feet of the present river level. The above examples illustrate the circumstances which prevail in the valley from its headwaters at Ulan to its junction with the Hunter River at Denman.

Tertiary Alkaline Rocks. There are several occurrences in the district of alkaline intrusive rocks which from their alkaline affinities and general characteristics have been placed among the Tertiary alkaline rocks occurring on the Eastern Highlands of New South Wales. There is a sheet-like mass of tinguaite situated on the floor of the

Wollar Valley near the village of Wollar. The eroded surface of the sill carries old river wash, which is approximately at the same level as the base of the Tertiary basalt flow on the western side of the valley.

Another occurrence of alkaline rock is at Barigan on the southern side of the area where the Wollar Creek heads in the Main Dividing Range. The valley at Barigan is a branch of the Goulburn Valley and of a similar type, with sandstone cliffs and talus slopes of Upper Coal Measures separated by alluvial flats up to half a mile in width. Mount Porcupine, one of the Barigan laccoliths, rises from the edge of an alluvial flat to a height of 1,000 feet, its denuded top being flanked on either side by low cliffs of Triassic sandstone. In this case the laccolith has been exposed by erosion of the valley, which is continuous with the general valley system of the district.

Old River Gravels of the Goulburn Valley. There are at least three old river levels of apparent significance, situated on the floor of the valley near the junction of the Munmurra and Goulburn Rivers. The old river beds occur at different levels above the present stream. One bed, situated some fifty feet above the present river level, contains river gravels and pebbles consisting of chert, hornfels, quartzite, and igneous rocks. The Barigan intrusions and Wollar Sill are well represented in various grades of tinguaite. The important feature in this bed is that no olivine basalt or dolerite has been found among its pebbles. A second series of river gravels occurs at a level about thirty feet above the present stream and contains practically all the rock types of the higher level, and in addition a limited quantity of olivine basalt. The third level is about fifteen feet above the present river, and contains many of the rock types already mentioned, as well as large quantities of olivine basalt and dolerite.

RELATION OF THE VALLEY TO THE SEDIMENTARY ROCKS.

From the general description of the different valley forms through which the Goulburn passes, it can be seen that there is a striking relation between the valley types and the nature of the strata in which they occur. Where the river is running entirely in sandstone strata it has cut a narrow gorge, but as soon as a shale formation makes its appearance near the river level the valley immediately opens out and assumes a mature aspect. The reverse of this procedure occurs when the river passes from a shale formation to massive sandstone.

Similar conditions are to be found in the valleys of the Cox and Grose Rivers, which exhibit wide valleys towards their headwaters where they are running in Coal Measure sediments, but pass into narrow gorges, developed in Triassic sandstone, along the lower parts of their courses. The Wollondilly River also passes from a wide valley into a narrow gorge where it joins the Warragamba. This geological control of valley types is particularly well illustrated in the case of the Goulburn Valley, as the river passes repeatedly from soft into hard formations, the change being accompanied in every case by a marked change in the valley form. Several possibilities have to be considered in explaining the contrasting valley types along the Goulburn River, but it seems evident that the different valley forms are all of the same age and belong to the same cycle of erosion, and that one of the main causes in the production of the contrasting types is the differential hardness of the strata through which they pass.

RELATION OF THE VALLEY TO THE GEOLOGICAL STRUCTURE.

Another feature which may have operated in the development of the Goulburn Valley is the up-warping of the strata where the gorges occur, involving local rejuvenation at places along the course of the river. There is a possibility of such rejuvenation on either side of the Wollar Anticline, but between the Mudgee-Cassilis road and Crowie, and along the Bylong-Sandy Hollow sections of the river, there seems to be less likelihood that local up-warping is responsible for the gorges. In each of these positions the sandstone overlying the shales in the valley walls dips below the river level to produce the gorges, the lowering of the sandstone being due to a north-easterly trend of the river bringing it up stratigraphically.

In the vicinity of the Wollar Anticline there would seem to be some evidence of local rejuvenation, as the basalts in the Wollar Valley are situated at least 100 feet higher above the present river level than the flow at Crowie, which is away from the influence of the fold. The part played by this rejuvenation in the development of the gorges on either side of the anticline would seem to be limited, since the maximum up-warping of the strata could be no more than 75 feet as the river is away from the crest of the fold, which has an amplitude of some 150 feet at the positions of maximum development in the gorges. Furthermore, if warping had been responsible for the full extent of the gorges, some evidence of rejuvenation would be expected at the point where the river cuts through the crest of the anticline, but at this point there appears to be no more rejuvenation in the valley than there is at either side near the troughs. It is probable that both differential hardness of the strata and the influence of warping have played a part in the development of the present topography in the Goulburn River district.

GEOLOGICAL AGE AND HISTORY OF THE GOULBURN VALLEY.

The close association of the Wollar Anticline and the long detour made by the Goulburn River to the north of Wollar strongly suggest that the two features are in some way connected. In considering this relationship, a very low gap which actually connects the Wollar and Wollara Valleys, and through which the Wollar-Bylong road passes, may be taken into consideration.(6)

At the position of the gap the Triassic sandstone has been removed completely from the ridge separating the two valleys, exposing the coal measure shales in which the gap, some 300 feet deep, has been developed. The road level in the gap is about 150 feet above the general level of the Wollar Valley and 200 feet above the Wollar Creek. It is important to note that the ridge in which the gap is situated occurs along the axis of the Wollar Anticline. The distance from the Wollar Creek to the Goulburn River through this gap is only six miles, while the river distance, round the long detour to the north, is almost forty miles. This gap may be due to the gradual widening of the valleys on either side, till the ridge between them became dissected, or it could indicate that the Goulburn River at one time flowed east through the break in the ridge.

The long detour which the river makes to the north, where it cuts through the lowest point on the crest of the plunging anticline before the structure becomes covered with the basalt of the Liverpool Range, strongly suggests that the river has been pushed slowly to the north, gradually sliding down the crest of the anticline as the folding developed. Additional evidence, however, shows that this

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(6) The gap is illustrated in the accompanying map (Fig. 3).

process could not have operated, as there is an outlier of Jurassic sandstone, standing slightly higher than the general level of the surrounding peneplain surface, situated on the anticline just to the south of the point where the river turns east through its crest. The presence of this residual means that the Goulburn River has not been pushed north by gradually sliding down the crest of the anticline. It is also evident that, if the river ever flowed through the gap in the ridge to the east of Wollar, the subsequent development of the anticline would have caused entrenchment of the river in the gap rather than push it to the north.

If the development of the fold has been responsible for the long northern detour made by the river, some process other than a gradual migration to the north must have been in operation. It would be possible to explain the facts by assuming that the river occupied its present course before the development of the anticline, and that the gap between the Wollar and Wollara Valleys is due to a gradual widening of both valleys till the ridge became dissected at the position of the gap.

An explanation which would allow the Goulburn to have passed through the gap and at a later stage have its course changed to the present position, would be one involving river capture occurring on the western side of the anticline, a tributary of the Munmurra having captured the Goulburn at its present junction with the Wollar Creek. There is, however, no conclusive evidence of river capture, and much more detailed physiographical work in the Goulburn River district is necessary before a satisfactory explanation of the river system can be made.

The age of the Goulburn Valley and the period at which it reached its present degree of development, are indicated to some extent by the physiographical evidence available, and upon its age depends an interpretation of the uplifting to which this section of the Eastern Highlands of New South Wales has been subjected since the close of the Mesozoic era.

The position occupied by the Tertiary olivine basalts in the Goulburn Valley places the major part of the valley development as pre-Tertiary basalt, and the presence of basalt flows in the comparatively mature valley indicates that the country was uplifted to an elevation of 1,500 to 2,000 feet at some period in the Tertiary era long before the advent of the olivine basalt. The condition at the base of the basalt flows in the valley suggests that the river possessed a mature valley floor at the time of their outpouring, and the proximity of the basalt to the present river level suggests that the country has not been subjected to any extensive uplifting since the outpouring of the basalts. The mature state of the present valley floor indicates that it has reached a degree of base-levelling equal to that which it possessed before the advent of the basalt flows, although it may have been rejuvenated to some small extent by post-basalt uplifting.

The occurrence of denuded alkaline intrusive masses in the Wollar and Barigan Valleys is of considerable significance. At Wollar there are Tertiary basalt flows situated on the sides of the valley which has denuded the Wollar Sill and the Barigan laccoliths. This situation requires the greater part of the development of the Wollar Valley to have taken place during the space of time which elapsed between the intrusion of the alkaline material and the outpouring of the olivine basalt flows at Wollar. These results are substantiated by the abundance of tinguaite and absence of olivine basalt in the highest level of the old river gravels near the junction of the Goulburn and Munmurra Rivers.

It follows that the tinguaites must belong to a very early series of Tertiary alkaline intrusives, and that the olivine basalts occurring on the side of the Wollar Valley, involving perhaps the entire Liverpool Range series, must all belong to the " Newer Basalts ".

It also seems evident that the antiquity of the valley depends on the ages of the alkaline intrusives and the " Newer Basalts " for limits to the period at which it reached a degree of development almost equivalent to its existing width and to at least two-thirds of its present depth. In this way it is indicated that the river is still running in a valley which commenced development at some time in the Tertiary era prior to the outpouring of the olivine basalts and after the intrusion of the alkaline rocks.

The exact effect produced upon the Goulburn River district during the uplifting of the Kosciusko Epoch is somewhat uncertain, due to incomplete evidence, but there seems to have been very little elevation. The fact that the basalt at Crowie, where no folding has occurred, is at least 100 feet nearer to the present river level than that in the Wollar Valley which is situated on the Wollar Anticline, may indicate differential uplift during the Kosciusko Epoch. This would mean that there has been some movement along the Wollar Anticline in post-basalt time, although the fold originated long before the basalt flows.

The fact that the Wollar Sill and Barigan laccoliths are situated in a general line along the crest of the Wollar Anticline suggests that the alkaline material was injected during the development of the fold. If this association is taken into account the age of the fold becomes limited to the period during which the alkaline rocks were injected, which must have been long before the outpouring of the olivine basalts.

In view of the Goulburn River district representing an area in which the Kosciusko Epoch had but little effect, it would seem to be more than a matter of coincidence that it should constitute one of the lowest saddles in the Main Dividing Range between Queensland and Victoria.

ACKNOWLEDGMENT.

In conclusion the writer wishes to acknowledge helpful discussion with members of the staff of the Geology Department, Sydney University, as well as members of the Geological Survey of New South Wales.

DERIVATIVES OF 9 : 10-DIHYDROANTHRACENE

By John Nevil Graves,
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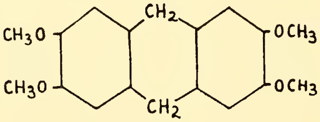
and Francis Lions, B.Sc., Ph.D.

(*Manuscript received, October 20, 1937. Read, November 3, 1937.*)

G. M. Robinson (*J.C.S.*, 1915, 267) has shown that veratrole can be condensed almost quantitatively with formaldehyde in presence of sulphuric acid to 2 : 3 : 6 : 7. tetramethoxy-9 : 10-dihydroanthracene (I) ; that the same substance can be readily obtained by treatment of homoveratryl alcohol with acid ; and that it is also obtainable by treatment of di-veratryl methane (II) with formaldehyde in presence of sulphuric acid. The condensation of veratrole with other aldehydes to the corresponding 9 : 10-disubstituted tetramethoxy dihydroanthracenes was not reported. It appeared to the authors that it might be possible to condense aldehydes with di-veratryl methane, so as to obtain 9-substituted tetramethoxy dihydroanthracenes, and a series of experiments was made in an endeavour to condense benzaldehyde with (II), and so to obtain 9-phenyl-2 : 3 : 6 : 7-tetramethoxy 9 : 10-dihydroanthracene (III). Under no conditions could this condensation be effected.



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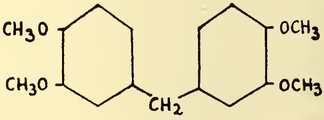

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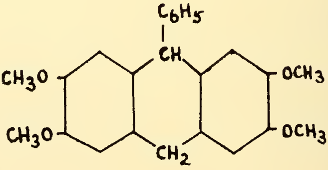
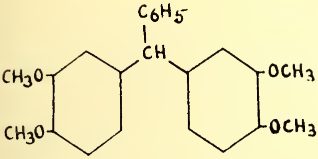


III.

Further efforts to prepare (III) were then made by first condensing benzal chloride with veratrole in presence of anhydrous aluminium chloride to phenyl di-veratryl methane (IV), and then endeavouring to react this with formaldehyde in presence of sulphuric acid so as to obtain (III). It was again found that condensation did not occur. Attempts were then made to prepare (III) by treating (II) with benzal chloride in presence of anhydrous aluminium chloride, but again without success.



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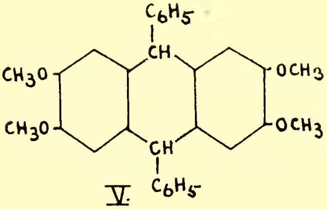


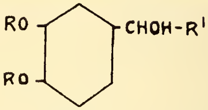
V.

The preparation of (I) from (II) with formaldehyde as described by Robinson (*loc. cit.*) was then attempted, but we were unable to prepare (I) by any variation of the experimental conditions. Unfortunately Mrs. Robinson did not give exact experimental details, and apparently we have been unable to reproduce the most favourable conditions. We propose to examine them more carefully later, and to try also the method of Stephen, Short, and Gladding (*J.C.S.*, 1920, 510).

It was observed that in the reaction of benzal chloride with veratrole in presence of anhydrous aluminium chloride, 9 : 10-diphenyl-2 : 3 : 6 : 7-tetramethoxy-9 : 10-dihydroanthracene (V) was also formed, in addition to (IV).

The triphenyl methane derivative (IV) is readily nitrated to the dinitro compound, a solid yellow crystalline substance melting at 204°. (II) is also readily dinitrated (Robinson, *loc. cit.*) to di(nitroveratryl) methane, but an attempt to reduce this to the corresponding diamine, with the ultimate aim of preparing 9 : 10-dihydro-2 : 3 : 6 : 7-tetramethoxy acridine, proved abortive.

Finally, it should be remarked that the great sensitivity of homopiperonyl and homoveratryl alcohols to acid, and the ready conversion of iso-eugenol methyl ether and of iso-safrole to dihydroanthracene derivatives suggests that secondary alcohols of the type (VI) which are readily accessible from protocatechuic aldehyde ethers via the



VI.

Grignard reaction, ought readily to form dihydroanthracene derivatives on treatment with acid ; experiments to study their behaviour have already been instituted.

EXPERIMENTAL.

Diveratryl methane (*II*) was prepared according to the method of Robinson (*loc. cit.*). Tetramethoxy benzophenone (veratroyl veratrole ; 50 g.), dissolved in boiling absolute alcohol (700 c.c.) was reduced by the fairly rapid addition of sodium (70 g.). The crude product distilled *in vacuo* at 255-265°/27 m.m. and crystallised after standing some time.

Attempted Condensation of Benzaldehyde and Di-veratryl Methane.

The following are typical experiments.

(*a*) Diveratryl methane (5 g.), benzaldehyde (2 g.), and anhydrous zinc chloride (5 g.) were heated together at 100° for four hours. The black tar was then extracted with ether and the ethereal extract eventually fractionated *in vacuo*. Benzaldehyde and di-veratryl methane were recovered unchanged. The residue after extraction was mostly zinc chloride.

(*b*) Di-veratryl methane (5 g.), benzaldehyde (2 g.), and zinc chloride (5 g.) were heated together at 160° for six hours. Worked up as before, benzaldehyde and (II) were recovered unchanged, and in addition some phenolic substance was obtained but it was not identified.

(*c*) Boiling together di-veratryl methane, benzaldehyde, and concentrated hydrochloric acid apparently did not lead to any condensation.

(*d*) Condensations attempted with anhydrous aluminium chloride as condensing agent caused only demethylation and much charring.

Attempted Condensation of Benzal Chloride with Di-veratryl Methane.

In a typical experiment di-veratryl methane (10 g.) and benzal chloride (6 g.) were dissolved in carbon disulphide

(50 c.c.). Powdered anhydrous aluminium chloride (10 g.) was then stirred in, the mixture assuming a deep magenta colour. It was finally refluxed gently for two hours, by which time hydrogen chloride was no longer being evolved. After removal of the solvent, cooling, and treating with ice and dilute hydrochloric acid, the oil which separated was taken up in ether and extracted with alkali. The dried ethereal solution was fractionated eventually *in vacuo*. Benzal chloride (4 g.) and di-veratryl methane (6 g.) were recovered. The only other obtainable products were phenolic bodies in the alkaline extract, presumably formed by demethylation.

Phenyl di-veratryl methane (IV) and 9 : 10-Diphenyl-2 : 3 : 6 : 7-tetramethoxy-9 : 10-dihydroanthracene (V). Veratrole (90 g.) dissolved in carbon disulphide (200 c.c.) was treated with powdered anhydrous aluminium chloride (20 g.). Benzal chloride (50 g.) was then added and the mixture heated under reflux until evolution of hydrogen chloride had ceased. The carbon disulphide was then removed and the residue decomposed with ice and dilute hydrochloric acid. The thick dark oil was taken up in benzene and extracted with alkali. The solvent was then removed from the dried benzene extract, and the residue fractionated *in vacuo*. The triphenyl methane derivative came over as a colourless viscid liquid at 245-250°/0·8 m.m. and solidified to a glassy resin. Whilst hot it exhibited a powerful blue fluorescence. Solutions of it in glacial acetic acid were straw coloured, with strong violet fluorescence. A bright scarlet colour was developed by the addition of concentrated sulphuric acid to the free substance or to its solutions. Eventually it was recrystallised from aqueous alcohol and was obtained in colourless needles (58 g.) melting at 124°. It could also be obtained in colourless needles from ligroin.

Found : C=79·0, H=5·9% ; calculated for $C_{23}H_{24}O_4$: C=79·6, H=6·2%.

The non-volatile residue left after distillation of (IV) was recrystallised from benzene. Colourless micro crystals melting at 308° were obtained. Analysis showed this to be (V).

Found : C=79·6, H=5·1% ; calculated for $C_{30}H_{28}O_4$: C=79·7, H=5·2%.

Phenyl di(nitroveratryl) methane. To a solution of (IV) (5 g.) in glacial acetic acid (20 c.c.), nitric acid (D 1·42 ;

5 c.c.) was added and the solution heated at 100° until crystals commenced to separate (about 20 minutes). The liquid was then diluted with water (70 c.c.) and the precipitated solid was collected, dried, and recrystallised from ethyl acetate. It came out in pale yellow prisms (6 g.) melting at 204°.

Found: $N = 6 \cdot 0\%$; calculated for $C_{23}H_{22}O_8N_2$: $N = 6 \cdot 2\%$.

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THE PYROLYSIS OF PHENYL CYCLOHEXENYL ETHER.

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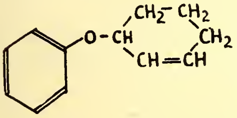
(*Manuscript received, October 20, 1937. Read, November 3, 1937.*)

It has been observed by Solonina (*Chem. Zentralblatt*, 1899, *1*, 248) that dibromo-derivatives of various hydrocarbons react with boiling 25% alcoholic sodium phenate solution, one bromine atom usually being removed as hydrogen bromide, leaving an olefine linkage, whilst the second bromine atom is replaced by phenoxyl. A diphenoxy hydrocarbon and diolefines may also accompany this unsaturated phenol ether as products of the reaction, and the relative amounts of each formed are to some extent governed by the relative positions of the bromine atoms in the original hydrocarbon.

Application of this reaction to 1 : 2-dibromocyclohexane has now shown that 3-phenoxy-Δ'-cyclohexene (phenyl cyclohexenyl ether, I), a colourless oil boiling at 135°/21 mm., with a pleasant odour recalling diphenyl ether, is formed in 60% yield, whilst in addition there can be isolated (*a*) hexahydrodiphenylene oxide (II), a colourless viscid liquid boiling at 157–8°/22 mm.; (*b*) o-cyclohexenyl phenol (III), a yellow oil of phenolic odour, boiling at 153–4°/22 mm.; and (*c*) a highly viscous liquid boiling at 220°/22 mm.



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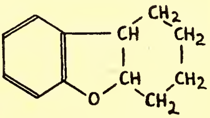

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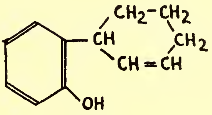
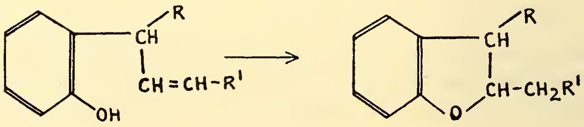


III.

The structure of the ether (I) was confirmed by an independent method of synthesis. Cyclohexadiene was prepared by heat treatment of 1 : 2-dibromocyclohexane with quinoline (*cf.* Crossley, *J.C.S.*, 1906, 1422). The cyclohexadiene obtained in this way contains cyclohexene (Harries and v. Splawa-Neyman, *Berichte*, 1909, *42*, 693). When treated with a solution of hydrogen bromide in glacial acetic acid it yields 3-bromo-△′-cyclohexene (Crossley, *loc. cit.*) containing some cyclohexyl bromide. When this crude product was refluxed with a solution of phenol in acetone in the presence of anhydrous potassium carbonate only the unsaturated bromide reacted, and 3-phenoxy-△′-cyclohexene, identical with the product already described, was produced. On oxidation with warm permanganate solution it was readily converted to α-phenoxy adipic acid, melting at 142°; and the identity of the products (I) prepared by both methods was confirmed in this way, the same acid being obtained from each.

A study of the pyrolysis of 3-phenoxy-△′-cyclohexene (I) showed that when (I) was heated fairly rapidly to 215° and maintained at this temperature for 3–4 minutes a reaction set in, and the temperature fell. If the external (bath) temperature was kept at 215° for a further five minutes and the product was then cooled and examined, it was found to consist of (*a*) a mixture of phenol and cyclohexadiene (50–60%); (*b*) hexahydrodiphenylene oxide II (15%); (*c*) o-cyclohexenyl phenol III (5%); and (*d*) a viscous, high boiling oil, probably a polymerisation product (20–30%).

The relatively high yield (15%) of the coumarane derivative (II) compared with that (5%) of the phenol (III) is worthy of comment. When phenol ethers of the phenyl allyl ether type are pyrolysed the amount of o-allyl phenol produced usually far exceeds the small amount of coumarane simultaneously formed (*cf.* Hurd, "Pyrolysis of Carbon Compounds", p. 215). The unexpected result in the example under discussion is readily explicable on stereochemical grounds. Examination of models shows clearly that coumarane ring closure of o-cyclohexenyl phenol is relatively easy compared with similar ring closures of the type.



Further, it was observed in one experiment that when an ethereal solution of (III) containing hydrogen chloride had been allowed to stand at room temperature for some time before being distilled, it was partly converted to a neutral substance melting at 68°, which could be separated from the phenol after distillation. This substance was found to have the molecular formula $C_{12}H_{14}O$, but the amount available was too small for further investigation. It was probably one of the stereoisomeric forms of (II). Cyclisation of o-allyl phenols to coumaranes by means of dry hydrogen chloride is well known (*cf.* Claisen, *Annalen*, *418*, 79, 83).

Von Braun (*Berichte*, 1922, *55*, 3761) claimed to have prepared hexahydrodiphenylene oxide (II) by catalytic hydrogenation of 2:2′-dihydroxydiphenyl. He described some derivatives, including a nitro derivative melting at 126°. However, Gilman, Smith and Cheney (*J.A.C.S.*, 1935, *57*, 2095) have shown that the derivatives obtained by v. Braun were, in fact, derivatives of 1:2:3:4-tetrahydrodiphenylene oxide, and have adduced evidence to show that the latter was present as an impurity in his product. Our compound, on nitration, gave a product which was evidently a mixture and melted indefinitely between 100° and 125°. Repeated recrystallisation did not improve the purity of this product, and the nitro-compound melting at 126° of v. Braun could not be isolated. It would thus appear that the product (II) is a mixture of stereoisomers, of which theory demands four.

The o-cyclohexenyl phenol (III) above described has been further characterised by preparation of its oxyacetic acid, melting at 143–4° (for method *cf.* Koelsch, *J.A.C.S.*, 1931, 304), and of its methyl ether, an oil boiling at 150–1°/22 mm. Warm permanganate oxidises this to α-(o-methoxyphenyl)adipic acid, melting at 179–80°.

EXPERIMENTAL.

Reaction between 1 : 2-dibromocyclohexane and alcoholic sodium phenate solution. A solution of sodium phenate was prepared from phenol (100 g.), absolute alcohol (300 ml.) and sodium (26 g.). To this solution 1 : 2-dibromocyclohexane (121 g.) was added and the mixture refluxed gently for 24 hours, moisture being excluded. At the end of this time the sodium bromide was filtered off, washed with alcohol, and the alcohol largely removed from the filtrate under diminished pressure. The residue was made alkaline with dilute sodium hydroxide solution and extracted with ether. The ether phase (Extract A) was dried over sodium sulphate. The alkaline phase was made acid with hydrochloric acid until it showed acid to Congo-paper, and the phenols were extracted with ether. The ether phase (Extract B) was also dried over sodium sulphate.

3-phenoxy-Δ'-cyclohexene (I). Extract A on distillation *in vacuo* gave a small lower fraction boiling at 100–120°/21 mm., consisting chiefly of unchanged 1 : 2-dibromocyclohexane. The next fraction was collected between 120° and 140°/21 mm., and contained the main product. This fraction was twice redistilled *in vacuo*, and was resolved into a lower fraction (10 g.) boiling at 125–133°/21 mm., and a main fraction (40 g.) boiling at 134–5°/21 mm. This latter is pure phenyl cyclohexenyl ether (I). A further quantity could be obtained by redistillation of the lower fractions.

3-phenoxy-Δ'-cyclohexene (I) is a colourless oil of pleasant odour, boiling without decomposition at 135°/21 mm.

(Found: C=82·3%, H=7·9%. Calculated for $C_{12}H_{14}O$: C=82·8%, H=8·1%).

Hexahydrodiphenylene oxide (II). After the fraction containing (I) had distilled, another fraction was collected between 150° and 165°/21 mm. This was redistilled and collected at 157–9°/22 mm., when 3 g. of a colourless viscid oil were obtained. The oil gave a deep red colouration with concentrated sulphuric acid. After another distillation it was analysed.

(Found: C=81·7, H=8·3%. Calculated for $C_{12}H_{14}O$: C=82·8, H=8·1%).

Product b.pt. 220°/22 mm. The final fraction in the distillation of extract A was a highly viscous oil boiling at 215°–225°/22 mm. This was redistilled and collected at 220–222°/22 mm.

o-Cyclohexenyl phenol. The distillation of extract B *in vacuo* yielded, firstly, a large quantity of ordinary phenol. When this had all distilled, a second phenolic substance (5 g.) was collected at 150–155°/20 mm. It was redistilled and collected at 153–4°/22 mm. It formed a bright yellow oil, having a faint odour resembling phenol.

(Found: C=82·7, H=8·2%. Calculated for $C_{12}H_{14}O$: C=82·8, H=8·1%.)

Product m.pt. 68°. In one experiment, when the extract B (which necessarily contains hydrogen chloride) was allowed to stand for some time before being distilled, the fraction boiling at 150–155°/20 mm. partially solidified. The solid was separated and recrystallised from a little benzene. It melted at 68° with softening, and was found to be a neutral substance. It gave, like (II), an intense red colour with concentrated sulphuric acid, and when warmed had a smell similar to that of hexahydrodiphenylene oxide (II). Analysis showed that it had the formula $C_{12}H_{14}O$.

(Found : $C=82{\cdot}7$, $H=8{\cdot}3\%$. Calculated for $C_{12}H_{14}O$: $C=82{\cdot}8$, $H=8{\cdot}1\%$.)

The small quantity available (0·3 g.) made extensive investigation impossible.

3-Phenoxy-Δ'-cyclohexene (second method). Cyclohexadiene was prepared according to the method of Crossley (*loc. cit.*) and from it 3-bromo-Δ'-cyclohexene was made following directions given in the same paper. This bromo compound contains cyclohexyl bromide, which it is impossible to remove by distillation.

Phenol (22 g.) in dry acetone (70 ml.) was treated with ignited pulverised potassium carbonate (36 g.) so as to form a suspension. The mixture was heated to boiling and crude 3-bromo-Δ'-cyclohexene (40 g.) added fairly rapidly. The flask was raised from the water-bath until the reaction had subsided ; the mixture was then refluxed (with calcium chloride guard-tube) for four hours, when the potassium salts were filtered off and washed with acetone. The acetone was evaporated from the filtrate, ether was added and the solution twice shaken out with dilute caustic soda solution. The ether phase was dried and the ether removed. The residue on distillation *in vacuo* fell into two fractions, one boiling at 70–80°/24 mm. and consisting mainly of cyclohexyl bromide, the other boiling at 135–140°/24 mm. The latter was again distilled and collected at 136–7°/24 mm., yield 10 g. This fraction had the characteristic odour of (I) and gave the same phenoxy adipic acid on oxidation. After another distillation it was analysed.

(Found : $C=81{\cdot}5$, $H=7{\cdot}9\%$. Calculated for $C_{12}H_{14}O$: $C=82{\cdot}8$, $H=8{\cdot}1\%$.)

Pyrolysis of 3-phenoxy Δ'-cyclohexene. The ether (10 g.) contained in a flask with ground-in air condenser, was heated fairly rapidly by means of a paraffin bath. The internal temperature was maintained at 215° for 3–4 minutes, when a reaction set in and the liquid boiled, the temperature inside the flask dropping sharply. The external temperature was kept at 215° for a further five minutes and the flask then cooled. (If the heating is continued for a longer time, no o-cyclohexenyl phenol can be isolated.) The contents of the flask were dissolved in ether and the phenols extracted by means of dilute sodium hydroxide solution. From the alkaline extract the phenols were recovered by acidification and extraction with ether. The neutral and phenolic ethereal extracts were dried over sodium sulphate.

The neutral extract gave on distillation *in vacuo* a small fraction (*ca.* 0·5 g.) boiling at 120–150°/22 mm. The main product then came over at 155–165°/22 mm. It was redistilled and collected at 157–9°/22 mm., and comprised a colourless viscid oil (1·5 g.). It was found to be identical with the hexahydrodiphenylene oxide (II) already prepared.

The phenolic extract when distilled *in vacuo* gave first phenol (3 g.) and then o-cyclohexenyl phenol (0·5 g.). The identity of the latter with the phenol (III) already described was established by analysis,

(Found : C=82·7, H=8·1%. Calculated for $C_{12}H_{14}O$: C=82·8, H=8·1%.)

and by comparison of the derived oxyacetic acids.

Oxidation of 3-phenoxy-$\triangle'$-cyclohexene. The ether (5 g.) was shaken with successive quantities of warm potassium permanganate solution until this was no longer decolorised. The product was made alkaline and filtered ; it was then concentrated to about 75 ml. on the water bath and acidified with hydrochloric acid. α-Phenoxy adipic acid separated out, and was obtained pure after one crystallisation from water with addition of decolourising charcoal. It formed colourless prisms melting at 142°.

(Found : C=60·6, H=6·1%. Calculated for $C_{12}H_{14}O_5$: C=60·5, H=6·1%.)

Dehydrogenation of Hexahydrodiphenylene oxide (II). Hexahydrodiphenylene oxide (1 g.) and selenium (2 g.) were heated at 290–300° (bath temperature) for eight hours. The product was dissolved in ether, washed, dried over sodium sulphate and distilled *in vacuo*, yielding an oil (0·5 g.). The presence of diphenylene oxide in this oil was proved by dissolving in carbon disulphide and treating with bromine. A solid resulted which after crystallisation from alcohol and petroleum ether melted at 195°. A mixed melting point determination with a sample of 3 : 6-dibromodiphenylene oxide m.pt. 195° (McCombie, McMillan and Scarborough, *J.C.S.*, 1931, 536) showed no depression.

Characterisation of o-cyclohexenyl phenol (III). The oxyacetic acid, *o-cyclohexenyl phenoxyacetic acid*, was prepared by the method of Koelsch (*loc. cit.*) and after two recrystallisations from water was obtained in colourless plates melting at 143–4°.

(Found : Equivalent, 232. Calculated for $C_{14}H_{16}O_3$ monobasic, equivalent 232.)

The methyl ether, *o-cyclohexenyl anisole*, was prepared by the action of methyl sulphate and caustic soda solution on the phenol. It formed a colourless oil boiling at 150–1°/22 mm. Oxidation of the methyl ether with warm permanganate was carried out in the same way as in the case of (I), and yielded α-(o-methoxyphenyl)adipic acid, which crystallised from water in colourless needles, m.pt. 179–80°.

(Found : Equivalent 133. Calculated for $C_{13}H_{16}O_5$ dibasic, equivalent 126.)

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THE STRUCTURE OF ORIGANENE.

PART I.

By ARTHUR JOHN BIRCH, B.Sc.

(*Manuscript received, October 20, 1937. Read, November 3, 1937.*)

Origanene was first isolated from the terpene fraction of Cyprus Origanum oil by Pickles (*J.C.S.*, 1908, 862), who assigned it the formula $C_{10}H_{16}$. He obtained from it a characteristic nitrosochloride and corresponding nitrolamines; bromine gave a liquid dibromide yielding p-cymene by the action of alkali; dry hydrochloric acid or hydrobromic acid gave a liquid mono hydrochloride or hydrobromide; hydration by means of dilute sulphuric acid gave terpin hydrate, while oxidation by means of perhydrol gave succinic acid. On the basis of this evidence he concluded that the substance is $\triangle 1:3$ p-menthadiene. The only objections obvious at the time were the production of terpin hydrate, and the comparatively low boiling point, but it has since been shown that this formula corresponds to the terpene α-terpinene, which possesses quite different properties.

The occurrence of the substance in the oil of *Origanum vulgare* has been confirmed by Rutovski, Guseva and Koroleva (*C.A.*, 1933, 5476), who isolated a nitrosochloride M.P. 75° C., and a nitrolpiperidine M.P. 184° C. Schimmel and Co. (Report 1922, 68) described the isolation of a new terpene from Spanish thyme oil, giving a nitrosochloride decomposing at 82°–84° C., a nitrolpiperidine M.P. 194°–195° C., and a nitrolbenzylamine M.P. 107°–108° C., which thus appears to be identical with origanene. A further occurrence was described (Schimmel's Report, 1930, 44) in the low boiling fraction of *Eucalyptus dives* oil, the characteristic derivatives noted above being obtained.* The substance was later isolated by Birch

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* This occurrence is not recorded in Chemical Abstracts, and the author wishes to thank Mr. A. R. Penfold for drawing his attention to it.

(This Journal, 1938, *71,* 54) from a sample of commercial α-phellandrene derived in all probability from the oil of *Eucalyptus dives.* It has now been isolated in larger amount from the same source, and its chemical properties examined with a view to determining its structure.

By careful fractionation and removal of α-phellandrene by means of its maleic anhydride addition compound, a fraction was obtained, B.P. 155°–160° C., which seems to be reasonably pure origanene, and which yields a larger amount of the crystalline nitrosochloride than any other fractions of the oil. The physical properties differ somewhat from those given by Pickles, the boiling point being lower, the refractive index lower, and the rotation higher. From these properties it seems very improbable that the substance is a monocyclic terpene as postulated by Pickles ; these substances usually possess a boiling point between 170° and 180° C., and a refractive index in the neighbourhood of 1·47–1·48.

Titration with bromine in glacial acetic acid confirmed the formation of a dibromide, showing the presence in the molecule of one double bond or two conjugated double bonds. The latter is improbable, as the substance does not react with maleic anhydride, and can be separated from α-phellandrene by the action of this reagent. Thus one double bond is present. Analysis of origanene and its derivatives by Pickles (*loc. cit.*) points to a formula $C_{10}H_{16}$, rather than $C_{10}H_{18}$, so it is probably a bicyclic terpene. This supposition fits in very well with the observed physical constants. It was not found possible to repeat the results of Pickles, in which he obtained terpin hydrate by the action of dilute acid, or p-cymene from the dibromide ; hydration was very slow, with production of only a small amount of high boiling liquid substances, while alcoholic potash on the dibromide gave mainly bromine containing compounds corresponding in boiling point to a monobromide, together with ketonic substances. The fraction corresponding to p-cymene was small, and could not be definitely identified as such. The production of terpin hydrate and p-cymene by Pickles may possibly be explained by the presence of impurities in his fraction. Since no derivatives of p-menthane or p-cymene have been definitely derived from origanene, there is still the possibility that it contains nine carbon atoms, as the analyses do not exclude this.

An examination of the nitrosochloride and the nitrolpiperidine in chloroform solution showed them to be optically inactive. This does not necessarily indicate the absence of asymmetry; pinene nitrosochloride as usually prepared is optically inactive even when prepared from the active substance.

Oxidation experiments yielded very little information; oxidation by means of perhydrol as described by Pickles gave only liquid acid products, no succinic acid being detectable, while dilute aqueous potassium permanganate gave a small amount of neutral ketonic substance, together with oxalic acid and liquid acids. The production of a ketone does not necessarily mean the presence of an extracyclic methylene group, as any glycol produced would be dehydrated under the conditions used. The liquid acid products gave no reaction with 2 : 4 dinitrophenylhydrazine sulphate, indicating the absence of ketonic acids, and, consequently, that the double bond does not terminate in a tertiary carbon atom.

An attempt was made to prepare the unsaturated oxime from the nitrosochloride by the removal of HCl, in the hope that it might be a known substance. Alcoholic alkali yielded only liquid products, while pyridine gave a small yield of a crystalline substance, M.P. 151° C. (micro N 8·1%; theory $C_{10}H_{14}$: NOH, N 8·5%). If this substance is the required oxime it does not correspond to any possible compound recorded in the literature.

In order completely to characterise origanene a number of derivatives were prepared from the nitrosochloride by the action of various amines. The nitrolmorpholine seems to be the best suited for characterisation, and it was accordingly carefully examined. Work on the structure of origanene is being continued.

Experimental.

Isolation of Origanene.

Commercial α-phellandrene (5 litres) was fractionated a litre at a time through a nine-bulb Golodetz column, the first 100 c.c. of distillate being collected each time. The combined distillate was then refractionated in the same apparatus, the fraction up to 59° C. (18 mm.) being collected. This was treated with maleic anhydride in acetone to remove α-phellandrene and refractionated, using a Widmer spiral. The following fractions were collected:

B.P. 765 mm.	Volume.	$N^{24°}_{D}$	$\alpha^{24°}_{D}$	Nitroso-chloride.
	c.c.			grm.
A. 145°–150° C.	10	1·4540	+12°·5	0·40
B. 150°–155° C.	7	1·4555	+13°·5	0·40
C. 155°–160° C.	10	1·4605	+12°·5	0·45
D. 160°–165° C.	8	1·4640	+8°·0	0·20

The isolation of the nitrosochloride was carried out on the four fractions side by side; alcohol (10 c.c.) and fraction (1·5 c.c.) were mixed, cooled in a freezing mixture to —15° C., and amyl nitrite (2 c.c.) added. Admixture of 4 c.c. of a solution containing equal volumes of concentrated hydrochloric acid and alcohol produced a momentary deep blue colour, followed by the appearance of a precipitate of colourless needles. This was filtered off, washed with 10 c.c. of alcohol, dried in a vacuum desiccator and weighed. M.P. 85°–90° C. (decomposes). Fraction C, giving the largest yield, must contain most origanene.

Bromine Value.

Fraction C (1·0 grm.) was mixed with glacial acetic acid (10 c.c.), and titrated with a solution of bromine in acetic acid containing one gramme to 50 c.c. Volume required, 56 c.c.; theory for one double bond is 59 c.c. A small amount of HBr was produced, so that substitution apparently accompanies addition.

Hydration.

Origanene (3 c.c.) was added to 5% sulphuric acid (50 c.c.) and the mixture left for nine days with frequent vigorous shaking. The unchanged oil was separated at the end of this time and distilled under reduced pressure. It consisted mainly of unchanged origanene, shown by the preparation of the nitrosochloride, and a small amount of higher boiling liquid from which no crystalline material could be obtained. The acid layer was saturated with ammonium sulphate, and extracted repeatedly with ether. No crystalline material was obtained.

Alkali on the Dibromide.

The dibromide was obtained by the addition of bromine to origanene in acetic acid solution, the mixture being poured into water and extracted with ether. It was thus obtained as a colourless viscous oil, which could not be induced to crystallise. The dibromide (4 grm.) was dissolved in excess of alcoholic potash (10%), and refluxed for one hour. Potassium bromide rapidly separated from the solution. The mixture was steam distilled, and the oil obtained (2 c.c.) fractionated under reduced pressure.

Fraction.	B.P.	Pressure.	$N_D^{22°}$
I	70°–85° C.	17 mm.	1·4890
II	85°–120° C.	,,	1·4935

Both these fractions gave the Beilstein halogen test, and both yielded amorphous red precipitates with 2 : 4 dinitrophenylhydrazine sulphate, showing the presence of ketonic substances. Fraction I was largely but not entirely oxidised by cold aqueous permanganate, so that a little p-cymene is probably present.

Alkali on the Nitrosochloride.

Origanene nitrosochloride (0·3 grm.) was added to 5 c.c. of a 10% alcoholic solution of caustic potash, and the mixture warmed until solution was obtained. Addition of water and extraction with ether yielded a pale yellow viscous oil, which could not be induced to crystallise.

Pyridine on the Nitrosochloride.

Nitrosochloride (0·4 grm.) was added to 3 c.c. of pyridine (carefully purified), and the mixture warmed. It was then poured into water, slightly acidified with acetic acid and extracted with ether. The oil so obtained deposited crystalline plates on standing, M.P. 151° C. (recrystallised from aqueous alcohol). Micro N, 8·1%.

Origanene Nitrosobromide.

This was prepared in an exactly similar manner to the nitrosochloride. Colourless needles m.p. 85° C. with explosive decomposition. Recrystallised by rapidly dissolving in chloroform, and precipitating with methyl alcohol.

Nitrolmorpholine.

Colourless prisms. M.P. 190° C. (uncorr.). C=65·5%, H=9·20%. The crystals belong to the orthorhombic system, the principal faces developed being pinacoids, prisms, and macrodomes, with pyramids in some cases. They show anisotropy, with high double refraction, an indefinite yellow interference colour being observed under crossed nicols.

Nitrolpiperidine.

Colourless prisms from methyl alcohol. M.P. 198° C. Micro N 10·9, 11·1%. Theory, 11·4%. Pickles gives M.P. 198° C., Schimmel and Co. give M.P. 194°–195° C.

Nitrolbenzylamine.

Colourless prisms from aqueous alcohol. M.P. 106° C. Pickles gives M.P. 104°–105° C., Schimmel and Co., M.P. 107°–108° C.

Nitroldiethylamine.

Colourless needles from aqueous alcohol, M.P. 140° C. Micro N, 11·6%. Theory, 11·8%.

Nitroldimethylamine.

Colourless needles M.P. 178° C.

Nitroldiisobutylamine.

Colourless needles M.P. 120° C.

Nitrol α Phenylethylamine.

Colourless needles M.P. 161° C.

Dibenzylamine on the nitrosochloride gave only a liquid product, and aniline yielded a brownish tar.

ACKNOWLEDGMENTS.

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ON THE OCCURRENCE OF GLENDONITES IN NEW SOUTH WALES, WITH NOTES ON THEIR MODE OF ORIGIN.*

By H. G. Raggatt, M.Sc.,
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(*Manuscript received, October 20, 1937. Read, November 3, 1937.*)

This paper deals mainly with the stratigraphical distribution of glendonites in the Permian sequence in New South Wales. This sequence, with the principal subdivisions and horizons referred to, are illustrated on page 337.

It should be noted that the term "Permian" as used in this paper is synonymous with the Kamilaroi of T. W. E. David. The reasons for regarding this sequence as Permian have been given in a recent paper.(13)

Review of Literature and Correction of Stratigraphical Position of some Previously Recorded Horizons.

The well known paper by David, Woolnough, Taylor and Foxall(6) gives a complete bibliography of previous work on glendonites, and records four occurrences in the Upper Marine series of the Permian System in New South Wales, as follows: (1) Glendon, (2) Singleton Railway Bridge, (3) Near Mount Vincent, (4) Huskisson.

These authors considered three of these horizons to be at stratigraphical intervals above the Muree beds of (1) 200 feet, (2) 1,000 feet, and (3) 700 feet. The Huskisson occurrence has been discussed by Dr. Ida Brown,(3) and is referred to below. As a result of geological work in the Hunter Valley during the years 1922–1930, the stratigraphical position of the three horizons referred to may be more accurately described than was previously possible.

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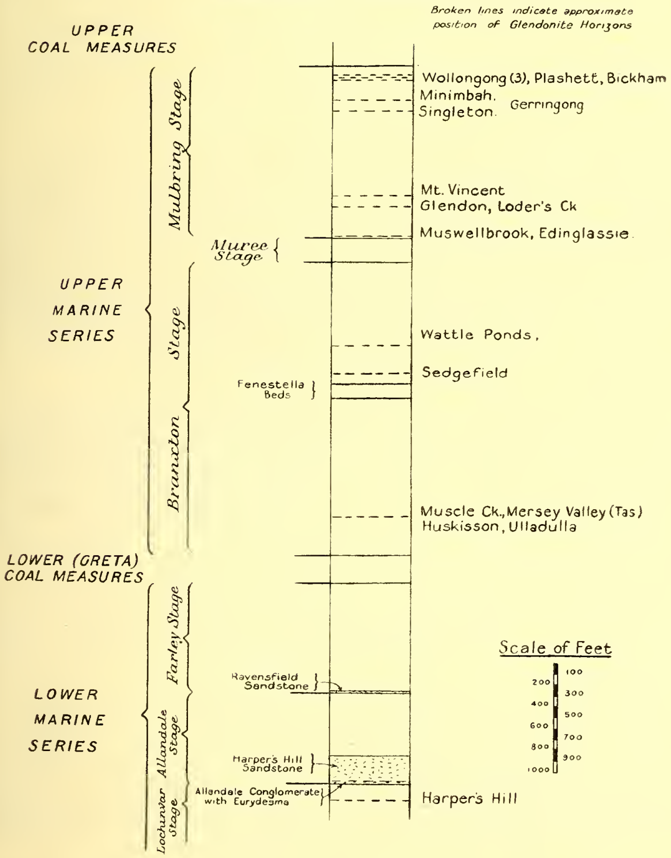
* Published by permission of the Under Secretary for Mines.

The Glendon horizon is on the western limb of the Belford Dome and is about 250 feet above the Muree beds. The Singleton occurrence lies in a syncline between the Loder and Sedgefield Domes, and is about 750 feet above the Muree beds.* So far as the Mount Vincent horizon is

STRATIGRAPHICAL COLUMN

of part of Permian Sequence in
Hunter Valley, N.S.W. showing
Glendonite Horizons



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* The structures referred to are illustrated and briefly described in a previous paper (Raggatt, H. G.(12).)

concerned, Mr. L. J. Jones places this at about 500 feet above the Muree (verbal communication).

In 1908, Carne⁽⁴⁾ recorded glendonites from two horizons in the Upper Marine Series at Muswellbrook, one, which he noted in Muscle Creek, 350 feet above the Greta Series, and one on the left bank of the Hunter River near the present railway bridge on the Muswellbrook-Merriwa line. The latter he thought to be 1,000 (?) feet above the Greta. (This record by Carne appears to have been overlooked hitherto.) The recent work indicates that the latter horizon is immediately above the Muree beds and about 1,600 feet above the Greta. The lower of these two horizons has previously been referred to as the Muswellbrook, but, if this is done, no suitable name remains for the higher. It is, therefore, proposed to name the lower the Muscle Creek and the higher the Muswellbrook horizon.

In 1910 Woolnough⁽²⁰⁾ recorded a glendonite zone in an argillaceous limestone bed of the Upper Marine Series in Wattle Ponds Creek adjacent to the Dyrring road, about three miles north from Singleton. Dr. Woolnough tentatively estimated this horizon to be 1,480 feet below the Muree. The recent detailed mapping of the Sedgefield Domes, however, indicates that this horizon is about 800 feet below the Muree, and about 2,000 feet above the Greta. (See also p. 342.)

Dr. Woolnough also found glendonites in the topmost beds of the Upper Marine Series at Wollongong in 1912. (See Walkom,⁽¹⁸⁾ p. 162). As the glendonites at this locality have not been previously described, and as geological excursions are frequently made there, some notes concerning it are given on page 339.

In 1911, Twelvetrees⁽¹⁶⁾ referred to the occurrence of glendonites in the Mersey Valley, at an horizon about 350 feet above the Tasmanian equivalent of the Greta coal measures.

Glendonites were recorded for the first time (in New South Wales) in a series other than the Upper Marine, by Walkom in 1913. This is the Harper's Hill horizon, which is in the Lochinvar Stage of the Lower Marine, about 150 feet below the Harper's Hill sandstone, and about 2,000 feet below the base of the Greta coal measures.

In 1925, Dr. Ida Brown⁽³⁾ published a note recording glendonites at Ulladulla. These she considers to be correlative with the Huskisson horizon, 100–200 feet below the base of the Nowra Grits, which are considered to be the equivalent of the Muree.

In 1932, Whitehouse(19) noted the occurrence of glendonites in the Dawson Valley, nine miles north-north-east of the village of Theodore. This constitutes the first record of the existence of glendonites in Queensland. They occur in a soft yellowish mudstone, which is a member of a fossiliferous marine sedimentary series overlying the Lower Bowen volcanics. The Dawson Valley glendonites have much in common with those from some of the well-known localities in New South Wales. No glacial erratics were observed in their vicinity.

New and Undescribed Localities in New South Wales.

During the course of field work, glendonites were found at a number of new localities. None of these occurrences shows any marked divergence in stratigraphical position from those previously known. Prefacing these descriptions some notes are given on the well-known but undescribed glendonites at Wollongong and Gerringong. The localities are described below in descending stratigraphical order.

Wollongong.

From the south side of Flagstaff Hill to the North Wollongong surf sheds the thickness of Upper Marine beds exposed in cliff sections and on the rock platform is about 100 feet. Of this thickness about 40 feet are exposed at the Flagstaff Hill, made up as follows:

Descending Order.

	Feet.		
	5	Sandy shale.	
	5	*Chœonomya audax* abundant	22 ft. sandy mudstone and sandy shale.
Upper Glendonite Horizon.	2	Numerous glendonites and concretions.	
	15	Sandy mudstone — fossils and erratics scarce.	
	8	Ferruginous argillaceous sandstone with discontinuous joints infilled with calcareous material; weathers spheroidally.	
Lower Glendonite Horizon.	6	Carbonaceous sandy mudstone. Concretions at top and glendonites two feet from base.	

The glendonites of the lower horizon occur as single individuals up to three inches in length, as groups of three or more such individuals, and as clusters of about an inch radius with as many as fifty small crystals in each cluster. Marine fossils and erratics are present in this bed, the largest erratic noted being one foot in diameter.

In the upper zone the glendonites are about 1½ inches in length, quite a large number consisting of an intergrowth of from two to four individuals. Glendonites form the nuclei of many of the concretions. The zone is fossiliferous, but erratics are scarce.

In addition to the exposures at the top of the cliff, the upper zone is also revealed on an almost isolated outcrop 200 yards easterly from the lighthouse. Here also the glendonites occur in groups with diameters up to five inches. In some instances, concretions have formed around the glendonites. A number of the concretions have iron pyrites arranged peripherally; in the others, pyrites appears to form the nucleus.

This zone, or one very close to it in stratigraphical position, outcrops on the rock platform about 100 yards north of the small beach at the boat harbour. The association of glendonites, fossils, and concretions is most marked at this point.

Eight chains northerly from the last mentioned outcrop, i.e. 15 to 20 feet higher stratigraphically, there are more glendonites and concretions, but as they are submerged at high water they are much eroded. Above this occurrence there are about 30 feet of arenaceous muds exposed, with abundant concretions and lenticular calcareous beds. There is a good cliff section and railway cutting through these beds at the south end of the North Wollongong beach.

It is difficult to determine accurately the stratigraphical position of the glendonites in relation to some known horizon such as the base of the Upper Coal Measures, since the dip is very gentle and the nearest outcrops of the Upper Coal Measures are about a mile away. Applying the observations made, to L. F. Harper's geological map of the area, and to the military contour map, the highest horizon of glendonites appears to be about 75 feet below the base of the Upper Coal Measures. As three glendonite horizons have been observed within such a small stratigraphical interval, and with such limited exposures, it is highly probable that many more such zones exist in the Upper Marine beds of this locality.

Plashett.

In Pringle's Saltwater Creek on the Plashett Holding, 3½ miles north-north-west from Jerry's Plains.

The glendonites occur at the top of the Mulbring beds (about 1,350 feet thick at this locality), and may be correlated with the uppermost of the Wollongong horizons. They are the small multiple variety, and are associated with *Chænomya etheridgei.*

Bickham.

Glendonites occur in blue mudstone on the right bank of the Pages River near the Bickham Homestead, 1¾ miles south-east from Blandford Railway Station. The glendonites are not plentiful, and consist mainly of single individuals or small groups. Fossils are present, but are not abundant.

The section of the Upper Marine Series in this area (Scone-Murrurundi) is markedly different from that exposed in the Lower Hunter. Measured with reference to the local equivalent of the Muree beds, the glendonite horizon is 250 feet above the top of that stage, but it is also very close to the base of the Upper Coal Measures, and is, therefore, preferably correlated with one of the Wollongong horizons.

Minimbah.

Good sections of the Mulbring beds can be examined in the railway cutting 2 miles north-west from Minimbah platform on the main northern railway. The glendonites occur about 850 feet above the Muree beds, and are thus on approximately the same horizon as the Singleton Railway Bridge occurrence. The glendonites are of the large type and occur both singly and in small groups. Both glendonites and marine fossils are particularly abundant at this locality. The glendonites occur in two zones about five feet apart, the lower ones being developed in groups, in close association with numbers of *Warthia micromphalus.* Other common fossils are *Stenopora crinita-ovata* and *Chænomya etheridgei.*

Gerringong.

It has been known for some years that glendonites occur at Red Bluff on the New South Wales coast 1½ miles northerly from Gerringong. Dr. Ida Brown informs me that the glendonites are in the Westly Park tuffs, and that they are the small multiple variety similar to those found at Wollongong.

Reference to L. F. Harper's geological map of the Gerringong district shows that the glendonites occur approximately 1,300 feet below the base of the Upper Coal Measures. Of this 1,300 feet, 900 are lavas. Hence the Gerringong glendonites appear to be approximately 270 feet below the lowest glendonites observed at Wollongong and may be correlated tentatively with either the Minimbah or the Singleton horizon.

Loder's Creek.

Seven miles south-westerly from Singleton. The glendonites occur on the main concretion horizon and, therefore, correspond to the type locality at Glendon. (Raggatt.(11)) *Stenopora crinita* occurs, associated with the glendonites, in a bluish-grey micaceous mudstone.

Edenglassie.

On the Edenglassie holding, six miles southerly from Muswellbrook in portion 77, Parish of Vaux, County of Durham. Only a few individuals were noted in a sandy shale.

It may be noted that the Muree beds are absent from the Upper Marine section over the greater part of the western limb of the Muswellbrook Dome, the total thickness of the Series there developed being not more than 1,600 feet. The glendonites occur 800 feet above the top of the Greta Series, and approximately at a stratigraphical position which is equivalent to the base of the Mulbring stage. They may be correlated with those originally noted by Carne in the Hunter River at Muswellbrook.

Sedgefield.

Glendonites were noted in a blue micaceous mudstone of the Branxton Stage in portions 37 and 38, Parish of Sedgefield, 1¼ miles north of the village of the same name. At first it was thought that these glendonites might be correlated with those originally noted by Woolnough at Wattle Ponds Creek, but as measurement indicates that they are 1,050 feet below the Muree beds this is improbable.

It will be observed that at five of the six new localities the glendonites occur in the top stage of the Upper Marine Series, namely the Mulbring beds.

Correlation of Horizons.

The method of correlation by reference to the stratigraphical interval above or below a known bed such as the Muree ([18], Fig. 2) may give an erroneous impression because it takes no account of the thickness of the containing beds at the various localities. Where this thickness is variable it is obvious that different correlations may be obtained depending upon the datum horizon selected. Dr. Ida Brown[3] has referred to this point in discussing the Ulladulla occurrence.

Another method of correlation that might be adopted is to express their position as a ratio between the interval of the horizon above or below a known datum, and some other factor such as the thickness of a stage. For this method to be exactly applicable, however, it would be necessary to assume that sedimentation was proceeding continuously, if unequally, at all the localities under consideration.

The correlations suggested in the foregoing brief description of new localities and on p. 337 take into consideration the general nature of the Permian sequence at each place, but it is not suggested that anything more than an approximate picture of their distribution in the stratigraphical column is given thereby.

The number of known glendonite occurrences in the Permian of New South Wales has increased so much during the past few years that it is almost certain that they are not referable to horizons which can be closely correlated from place to place.

On p. 337 average thicknesses of the formations as they are developed in the Lower Hunter Valley are given, and the correlations with localities outside that area, namely Wollongong, Ulladulla, Mersey Valley (Tasmania) are approximate only. They cannot be otherwise. Dr. Ida Brown's correlation between the Huskisson-Ulladulla and the Muscle Creek horizon is accepted.

Twelve horizons are represented, eight of which are in the Mulbring Stage, three in the Branxton Stage, and one in the Lower Marine Series. This may not give quite a true picture of the distribution of glendonites for several reasons. The Lower Marine Series has not been examined in detail for many years, and the beds of the Upper Marine below the Fenestella shales are exposed over only a relatively small part of the area occupied by beds of Permian age in the Hunter Valley. Further, in geological mapping it is the upper and lower parts of the Mulbring beds which receive most attention, the latter because of their nearness to a recognisable key horizon, the Muree Stage, and the former because of the economic importance attaching to the delimitation of the base of the Upper Coal Measures as accurately as possible. It may well be, therefore, that new horizons of glendonites will be found in the course of future field work.

CONDITIONS OF FORMATION OF GLENDONITES.

David, Woolnough, Taylor and Foxall(6) summarised the results of their research under ten headings. The majority of these are in support of their principal conclusion that glendonites are formed under marine conditions and are pseudomorphous after glauberite (i to iv, ix and x in part). This conclusion has been well supported by later work, but certain others relating to their mode of origin have been somewhat modified.

These authors considered that "The fact that the longest axes of the pseudomorphs trespass across the planes of lamination in the mudstone and have flattened themselves at their extremities where they grew against a coral or pebble; and the fact too that they sometimes enclose fossil brachiopod shells implies that they were not originally developed upon the surface of the mudstone (where their crystallographic force would have enabled them to have displaced small objects, as small pebbles and brachiopod shells) but at some depth below the surface".

In the first place the transgression of the bedding-planes by the long axes of the glendonites does not prove the intrusion of the former by the latter. This would appear to be the case whether it had actually happened or the glendonites had simply grown at the surface and become covered by the later sediments. The same might be said of any small object with a vertical dimension greater than the distance between any two bedding-planes.

In the second place the relationship existing between the glendonites and other objects such as pebbles and shells might be expected to arise whether the glendonites grew at the surface or beneath it. A crystal growing under quite normal circumstances would enclose or grow around any considerable object it might encounter, and if this process were arrested for any reason whatsoever, it would appear to terminate against such object. Obviously, where a number of crystals are growing in the same environment, there must be examples showing all stages in such an enveloping process. The principles controlling the growth of crystals are well set out by Taber,(14) and as bearing on the present inquiry the most important is as follows : " Most crystals are unable to overcome external pressure resisting growth because there is no provision for supersaturating the solution with respect to the faces that are under pressure and that are thereby rendered more soluble."

Therefore, the fact that glendonites enclose fossils or terminate against them does not appear to support the view that glendonites necessarily formed at some depth below the surface of the muds in which they are found. It has been pointed out elsewhere that glendonites form the nuclei of small discoid concretions on the main glendonite horizon of the type locality ((11), p. 150), and it has been shown above that glendonites form the nucleus of concretions at other localities, as at Wollongong. Concretions showing well marked zoning are exposed in the railway cuttings two miles north-westerly from Minimbah platform. A small group of glendonites occurs between two zones of growth in one of these concretions. If the author(11) has succeeded in proving that the concretions are contemporaneous, then the glendonites must have been formed contemporaneously also.

David and others(6) have suggested that (No. x) " possibly sulphate-forming bacteria may have existed in the black muds of the matrix ", and these authors also refer elsewhere to the glendonites occurring in every case in " a dark grey, rather carbonaceous mudstone " (No. vii), a statement which is true in a general way of the new localities, though the mudstones are typically calcareous, and blue or grey depending largely upon the freshness of the exposed surface. Fresh exposures and bore cores are almost invariably blue in colour. It is also true, however, that apparently exactly similar beds contain no glendonites. Bacteria may certainly have played their part, but there is no reason for supposing that they may have been any more active at these horizons than at many others of similar lithology which are barren of glendonites.

Dr. Ida Brown ((3), p. 29) states that " it is noteworthy that where glendonites occur . . . abundant fossils are frequently associated with them ". She considers the sulphur necessary for the formation of glauberite " may have been derived from the decomposition of the soft parts of the abundant marine organisms with or without the aid of bacterial action ". The reference to the presence of marine organisms in abundance is borne out at only one of the new localities recorded in this paper, but fossils certainly do appear to be present wherever glendonites occur; and, moreover, where the fossils are abundant the glendonites are plentiful, where the fossils are not common, there are few glendonites. Of course there is not necessarily any causal connection between these facts.

The association of glendonites with concretions and the alternations of these in zones has been stressed before. In regard to these it was pointed out ((11), p. 156) that it is generally agreed that the amount of calcium carbonate held in solution by the waters of the ocean approximates saturation, at least in the warmer seas, and that the actual quantity of calcium carbonate held in solution at any time varies inversely as the temperature. On the other hand deposits of glauberite forming at the present time (as in the Gulf of Karabughaz) are thicker in winter than in summer (Twenhofel,(17) p. 367).

If, therefore, one assumes a shallow arm of the sea the waters of which have reached saturation with respect to calcium carbonate under very cold conditions, slow warming is all that is necessary to induce the deposition of the calcium carbonate which forms the concretions. A renewal of cold conditions would lead to cessation of such deposition, and in extreme cases to the death of numerous organisms. This might be a local phenomenon and might be brought about by the advent of floating ice. The presence of numerous glacial erratics is clear evidence that ice rafts had access to arms of the sea in many places, but it may readily be supposed that bars precluded this happening in others.

Such conditions would be favourable for the formation of glauberite, the decomposition of the soft parts of marine organisms perhaps providing sulphur, and the cold conditions favouring the deposition of glauberite as in the Gulf of Karabughaz. The close association of glendonites with marine fossils over limited areas, e.g. with *Warthia* at Minimbah, supports this hypothesis.

Intermittency in this process would give rise to the alternating succession of concretion and glendonite zones observed in some localities, and to the formation of calcareous concretions with glendonites as nuclei.

This explanation is open to the objection already mentioned, that beds containing abundant fossils and apparently similar lithologically to those in which the glendonites occur are barren of the latter, and that with such a relatively simple mode of origin it is perhaps curious that glendonites, which have been recorded from so many localities in New South Wales, are of rare occurrence in beds of similar geological age in other States of the Commonwealth. (The writer has recently had the opportunity of examining much of the Permian in North-West Basin, Western Australia; no glendonites were noted.) It must be borne in mind, however, that the origin postulated requires a rather nice adjustment between the degree of concentration of the necessary salts and temperature, and that in any case the objection is a negative one.

It is worth while reiterating that there is a concentration of glendonite occurrences in the Mulbring Stage, and particularly towards the top of that Stage. This may be interpreted as being due to the fact that the Upper Marine sea was becoming shallower and divided into more or less isolated basins with approach to Upper Coal Measure time, its salts more concentrated, and chemical equilibrium in its waters more readily liable to be upset by temperature changes.

PERMIAN GLENDONITES AND CRETACEOUS PSEUDOMORPHS.

The evidence afforded by the Permian glendonites suggests that they can be expected to occur only on fossiliferous horizons in marine glacial deposits. Apart from the Permian the only other beds in New South Wales which satisfy these conditions are the Cretaceous of the Great Artesian Basin. These beds, which outcrop typically at White Cliffs and Tibooburra, are now considered to be glacial (Andrews,(2) p. 96; Kenny,(19) p. 99). In them occur the "fossil pineapples" first recorded by Jaquet ((8), p. 141). These, Anderson and Jevons ((1), p. 34) consider to be opalised pseudomorphs after glauberite.

The authors ((6), pp. 5 and 6) of the 1905 paper on glendonites referred to the White Cliff pseudomorphs, and in 1926 David and Woolnough ((7), pp. 346–347) put forward the occurrence of pseudomorphs after glauberite as "possible evidence of the seas having been cold in Australia in Cretaceous time". and in his Explanatory Notes, David (1932, p. 84) states that the pseudomorphs

" resemble the glendonites associated with erratics in the sediments of the cold Middle Permian seas of Australia ".

So far as can be observed, the only difference between the pseudomorphs from the Permian and those from the Cretaceous is their present chemical composition. Groups of glendonites may be seen at several localities in the Hunter Valley and at Wollongong which are very similar to the figures published by Anderson and Jevons, and Ida Brown (*loc. cit.*) has described glendonites from the South Coast as occurring as a dozen or more individuals. (Compare Plate XV, *Proc. Linn. Soc. N.S. Wales*, Vol. 7, Part 2, and Plate XI, *Rec. Austr. Mus.*, Vol. VI, No. 1.)

Having regard to the fact that opalised shells are found in these deposits, the Cretaceous pseudomorphs may have suffered two changes, the first early in their history when the glauberite was replaced by calcium carbonate, and the second in Tertiary or later times when they became opalised.

It is probably significant that erratics and opalised fossils are associated with the pseudomorphs at White Cliffs. Mr. Kenny has compiled a list of these fossils which the late W. S. Dun states are all shallow water forms. (See also Pittman(10) re association of pseudomorphs and fossils.) The Cretaceous " glendonites " thus appear to offer rather striking confirmation of the conclusions reached regarding those from the Permian.

SUMMARY.

The stratigraphical position of a number of previously mentioned glendonite horizons has been defined, and six new localities have been briefly described.

The paper is believed to constitute a complete record of glendonite occurrences in Australia.

Glendonites are known to occur on at least twelve horizons in the Permian in New South Wales, and no less than seven of these are in the Mulbring Stage of the Upper Marine Series. It is considered that this indicates that the Upper Marine sea was becoming shallower and divided into more or less isolated basins as Upper Coal Measure time was approached. This led to concentration of salts, with the result that chemical equilibrium in its waters was more readily liable to be upset by temperature changes than previously.

The presence of numerous erratics shows that glendonites were formed, at least in many instances, under cold conditions, and the absence of erratics from some places is

readily explained under the above conditions by the presence of bars.

The alternation of calcareous concretion and glendonite horizons in many places is commented upon in the light of the information given in the preceding paragraph, and the fact that the solubility of calcium carbonate has an inverse, and of glauberite a direct, relationship to temperature.

The similarity, referred to previously by other authors, between the pseudomorphs in the Cretaceous at White Cliffs and the glendonites in the Permian is stressed, and it is suggested that their mode of origin was similar.

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NOTES ON THE STRATIGRAPHY AND PHYSIOGRAPHY OF THE TALBRAGAR "FISH-BED" AREA.

By J. A. Dulhunty.

(With two text-figures.)

(*Manuscript received, October 18, 1937. Read, December 1, 1937.*)

Introductory.

The Talbragar Fossil Fish Beds are situated 20 miles north-east from Gulgong on Portion No. 14, Parish of Bligh.

The general stratigraphy of the area surrounding the Fish-Beds is described in the present paper, with a view to elucidating the relation which the fossiliferous cherty shales of the Fish-Beds bear to the associated strata.

The physiography of the area is also important as it is intimately connected with the physiographical development of the Merriwa-Ulan district, described by the present writer in a previous paper (This Journal, 1937, *71*, 297).

Topography.

The principal topographical feature is the Main Dividing Range, trending approximately north-east to south-west across the area, and consisting of a low ridge or slightly elevated portion of the old peneplain surface which extends to the east and west. The average elevation of the Dividing Range at this particular point is some 1,800 feet above sea level.

The peneplain surface has been developed in sandstone strata and now forms a plateau extensively dissected by shallow and mature valleys carrying the headwaters of the Goulburn River on the east and the Talbragar River on the west. The floors of these valleys lie some 300 feet below the plateau surface.

Basalt-flows have produced rounded hills which stand out above the general surface, as at Cockabutta Mountain. These flows are olivine-basalt of late Tertiary age, and in several places occupy positions on the sides of the valleys, indicating that the major part of the valley development antedated the Kosciusko Uplift. In addition to the mature nature of the valleys and the occurrence of Tertiary basalt on their floors and sides, the streams at their headwaters are running sluggishly in the alluvium of their flood-plains, and show no renewed activity such as would be expected at the actual divide on the Eastern Highlands. The Talbragar River near Cockabutta Mountain and the Goulburn River near Ulan, each no more than three miles from the Main Divide, both possess valley-floors over a mile in width carrying extensive deposits of alluvium situated a few feet above the present river levels.

These facts suggest that the area lagged behind during the Kosciusko Uplift, and they may be correlated with similar evidence in the country lying to the east, where an uplift to an elevation of 1,500 to 2,000 feet early in the Tertiary Era is indicated.

The slightly elevated ridge which forms the actual divide is of tectonic rather than erosional origin, as the sandstone strata on the western side dip to the north-west at a very low angle, while immediately to the east of the range the dip assumes a north-easterly direction. The crest of this anticlinal structure plunges at about 0·5° in a direction N. 20° E. The age of the anticline is limited to early Tertiary or perhaps late Mesozoic, as the streams dissecting it possess the degree of maturity already described, and the fold itself contains early Mesozoic strata.

In the south-western corner of the area the topography changes from the mature sandstone type to one of mature granite aspect, due to the presence of a much denuded granite bathylith. The change occurs about three miles to the south-west of the Fish-Beds, the plateau ending in low sandstone cliffs and broken slopes, from beneath which the granite emerges to form a mature surface some 350 feet below the plateau level. This rises gradually to the south-east for about nine miles until it reaches the general level of the plateau. The granite surface appears to represent the general topography of a sea-floor along the shore-line of a late Permian sea.

The granite, from which the overlying sediments have comparatively recently been removed, is much decomposed, boulders many feet in diameter being quite soft and weathered throughout. This feature would suggest that during Permian time a preliminary decomposition commenced, which was later arrested by the drying of the sediments, and finally recommenced in Tertiary time on the removal of the shore-line deposits.

STRATIGRAPHY.

From an examination of the strata and outcrops between the Fish-Beds and the granite to the south-west, the general sequence and thickness of the beds in the area are as follows :

		Feet.
Jurassic	Munmurra sandstone	150
Triassic	Comiala shales	35
Triassic	Wollar sandstone	250
Kamilaroi ..	Upper coal measures (shales) ..	65
	Upper marine (sandstone) (?) ..	40

The outcrop of these beds and their distributions are illustrated in the accompanying map (Fig. 1) of the area.

All the beds are conformable and have a dip W. 11° N. at 0·75° in the vicinity of the Fish-Beds, while the dip approaches north-west on the northern side of the area, and on the eastern side of the Main Divide it becomes approximately N. 40° E. at about 1°. The beds thicken fairly rapidly as they pass to the east and north from the old granite shore-line, giving the section indicated in Fig. 1.

The lowest bed, lying on the granite to the south-west of the Fish-Beds, consists of some forty feet of fine sandstone, which from its position and lithology has been classed as Upper Marine.

The basal sandstone is followed by about sixty-five feet of Upper Coal Measure sediments containing *Gangamopteris*, *Vertebraria* and *Phyllotheca*. These beds are typical Permian deposits consisting of carbonaceous shales, white chert and soft sandstone bands, as well as several carbonaceous outcrops suggesting bands of weathered coal. The Permian beds are continuous with the Upper Coal Measures on the eastern side of the Main Dividing Range. Permian beds undoubtedly continue to the north, but their extent cannot be determined readily on account of the thick covering of Mesozoic sediments.

The Triassic series, continuous with the Wollar Sandstone to the east, consists of massive beds of coarse white sandstone packed with small quartz pebbles so as to form a kind of fine conglomerate. The conglomeratic nature of the rock is accentuated towards the base of the series, while the topmost beds constitute a more normal sandstone. The Triassic sandstone is followed by a band of grey and blue shales continuous with the Comiala Series occurring

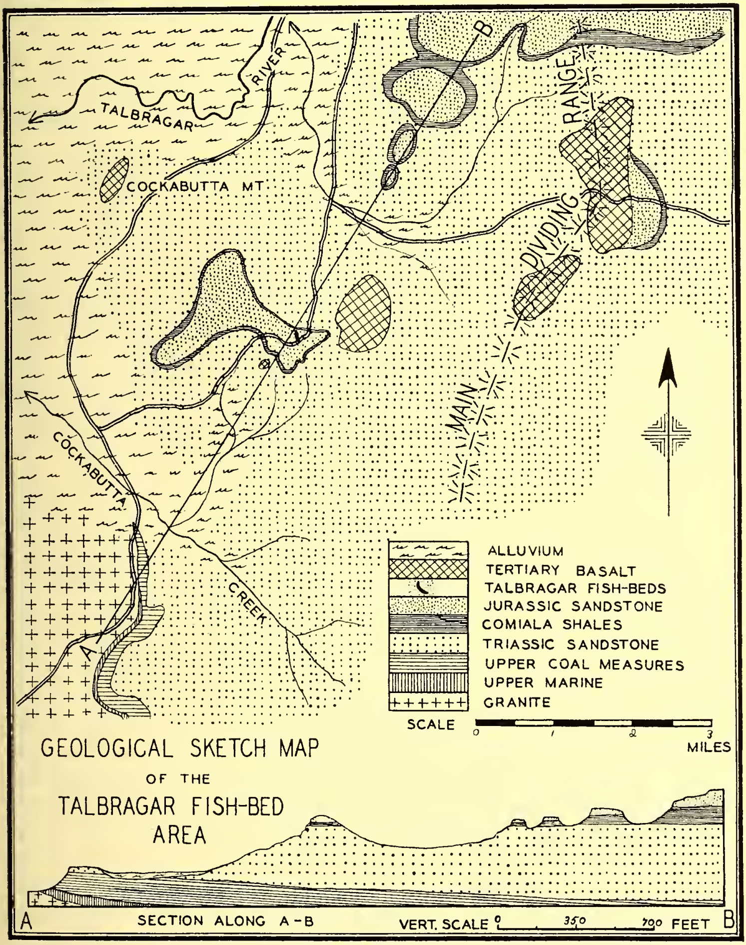

Fig. 1.

on the eastern side of the Main Divide in the Merriwa-Cassilis district. In the vicinity of the Talbragar Fish-Beds, the shales occur as outliers having a maximum thickness of about thirty-five feet, but are rather irregular, thinning in places to less than fifteen feet. The band thickens as it passes to the north until it reaches a thickness of some seventy-five feet, when the outliers give place to a continuous horizon which passes over the Main Divide, reaching a maximum thickness in the Comiala Series of 210 feet, some twenty miles to the north-east. The beds consist essentially of non-tuffaceous mudstones and clay-shales with some ferruginous bands, but on passing to the north-east they develop a tuffaceous nature, which becomes quite pronounced and constitutes a general feature of the Comiala Series.

The shales are followed by a massive red and yellow Jurassic Sandstone, of a coarse and porous nature, which can be correlated with the Mumbedah Beds occurring in the Dunedoo-Binnaway district, described by Mr. E. J. Kenny (*Annual Report Dept. Mines, N.S. Wales*, 1934). The Jurassic sandstone forms protecting caps to the outliers of Comiala shales in the vicinity of the Talbragar Fish-Beds, reaching a maximum thickness of some 200 feet on the northern side of the area, where it passes over the Range. It is continuous with the Munmurra Beds, an extensive Jurassic sandstone formation overlying the Comiala Series in the Merriwa-Cassilis district.

THE FISH-BEDS.

The fossil fishes occur in hard ferruginous and siliceous chert or cherty shale, which is crowded with well-preserved plant remains. The chert is situated on the north-eastern side of Farr's Hill, which is an outlier of Comiala shales and Munmurra sandstone carrying the residual of an olivine-basalt capping.

The outcrop of the Fish-Beds consists of loose blocks of chert protruding through the basalt alluvium on the side of the hill. The chert does not occur along any definite horizon, nor does it form a continuous outcrop, but appears as isolated patches of broken rock lying in the alluvium on the hillside. These are situated in relation to the contours of the hill in such a way as to suggest an outcrop which assumes a curve extending downwards from the top of the hill, passing obliquely across a gentle slope, and then running almost horizontally for three chains, when it terminates abruptly. Both the quantity of the chert and the size of the blocks increase as the line of outcrop passes down the side of the hill, reaching a maximum at its lowest point. The isolated sections of the outcrop are separated by as much as two chains of alluvium in which there is no sign of the chert.

The outcrop of the Comiala shales and Munmurra sandstone is somewhat obliterated by alluvium on the north-eastern side of Farr's Hill, but the lowest point on the curved line of outcrop of the Fish-Bed chert is a little above the horizon occupied by the Comiala shales. It is evident from the floating nature of the Fish-Bed chert that the blocks must have moved down the hill considerably from their original position, and, taking this fact into consideration, it is estimated that the lowest point on the Fish-Beds is about thirty feet above the top of the Comiala shales, and is separated from them by a similar thickness of Jurassic sandstone.

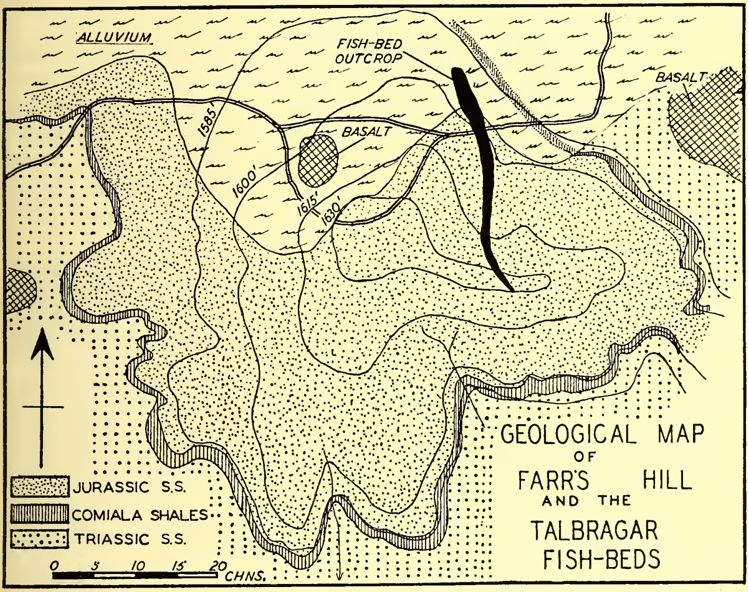

Fig. 2.

Horizontally-bedded Jurassic sandstone occurs on both sides of the curved line of outcrop made by the blocks of chert, as illustrated in Fig. 2. The position of the sandstone, apparently overlying as well as underlying the chert, suggests that the Fish-Beds as a whole form an isolated body lying in the horizontally-bedded Jurassic sandstone.

The actual structure of the Fish-Bed chert body constitutes a complex problem. It was originally suggested by Professor David and E. F. Pittman that the beds formed a capping to the hill, the chert lying on horizontally-bedded Triassic sandstone. (*Mem. Geol. Surv. N. S. Wales, Pal.* No. 9, 1895). This conception required a thickness of at least 40 feet of chert.

It has now been established, as mentioned above, that the sandstone associated with the Fish-Beds is of Jurassic age, and that horizontally bedded sandstone overlies as well as underlies the chert beds, reducing their possible thickness to no more than twenty feet. With this additional evidence the conception of the chert beds forming a capping to the hill would not appear to explain fully the structure of the deposit.

It has been suggested by Professor Browne and Mr. L. L. Waterhouse that the discontinuous nature of the outcrop, seen in patches of broken chert appearing at different levels along the line of outcrop which swings up the side of the hill, may be indicative of some type of step-faulting. Faulting would explain the peculiar nature of the outcrop, but it is difficult to obtain any conclusive information owing to the thick covering of alluvium on the side of the hill.

An alternative suggestion made by the writer is that the line of outcrop of the chert may represent a section of a comparatively thin lake-bed deposit on the side and bottom of a basin-shaped erosion hollow in the Jurassic sandstone, which subsequently filled with sands similar to those forming the outer walls of the basin. This suggestion would require an unusually deep erosion hollow considering the conditions of sedimentation which must have existed during the deposition of the Jurassic sandstone, and it would also mean that the major portion of the basin deposit has been removed during the development of the present topography.

THE ESSENTIAL OILS OF EUCALYPTUS AUSTRALIANA (BAKER AND SMITH) AND ITS PHYSIOLOGICAL FORMS.

PART II.

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(*Manuscript received, October 21, 1937. Read, December 1, 1937.*)

In our previous paper* we dealt with the essential oils of *Eucalyptus australiana* obtained from foliage collected in New South Wales. We had already investigated the essential oils distilled from the leaves and terminal branchlets of this species growing in Victoria, but decided to withhold publication of the results until a later date in order to obviate confusion. Mention was also made on page 116 (l.c.) that the botanical characters of the species *Eucalyptus australiana*, and its varieties, would be dealt with in a subsequent paper to be published conjointly with Messrs. E. Cheel and M. B. Welch. The work is not yet ready for publication, but the recent issue of a book entitled " The Call of the Koala " by Ambrose Pratt, compels us to submit the results of a preliminary investigation of Victorian trees for early publication.

The following statement appears on page 56 of Mr. Ambrose Pratt's book :

" An examination of the species of Eucalypts regularly fed to our Koalas arraigned the common peppermint gum (*E. australiana*) as the most likely culprit. The leaves of this gum contain 3·5% of oil, and of this more than half consists of cineol. The peppermint gum has an incomparably greater total oil content and a much higher proportion of cineol than any other Eucalypt used by the Victorian Koala race. . . .

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* THIS JOURNAL, 1935, *69*, 111-122.

" . . . . Until more is known of the Peppermint Gum and the chemical changes it undergoes at different seasons, and under diverse conditions of soil and climate, it must be labelled dangerous, and it should be banned from all zoos."

The accompanying table shows that *E. australiana* growing in Victoria consists of a number of varieties whose essential oils differ considerably in chemical composition from those of *E. australiana* growing in New South Wales.

This is the first record of the occurrence of piperitone in quantity in any tree belonging to the *E. australiana* group. The results of the examination of the oil from *E. amygdalina* collected at New Norfolk, Tasmania, have been included in the table for comparison. It is of interest to note that the composition of the oil of *E. australiana* growing at Crystal Creek, Alexandra, about 100 miles from Melbourne, is in fair agreement with the composition of the oil distilled in New South Wales, i.e. large quantity of cineol with absence of phellandrene when tested by the usual nitrite tests of the United States and British Pharmacopœias. The low cineol content of the oil from this tree is due to the unusual nature of the foliage and the fact that it was of adventitious growth, aged four months.

A comparison of the essential oil of *E. amygdalina* obtained in Tasmania showed marked agreement with the essential oil from one of the Victorian varieties of *Eucalyptus australiana*. This raises the vexed question of the botanical nomenclature of the species ; we wonder whether it would not be advisable to simplify the nomenclature by correlating all species of *E. australiana* and its varieties with *E. amygdalina*. The name *E. amygdalina* could be restricted to the Tasmanian tree and this would accord with the views of the majority of botanists. The mainland trees could be regarded as varieties of this species. Botanical material of all the foliage distilled were submitted to Mr. E. Cheel, who reported as follows, viz. :

" The Victorian series of specimens are somewhat different from those of New South Wales, but the characters are not sufficiently distinctive to enable one to separate them from the type specimen of *E. radiata* (Sieber)."

E. radiata of Sieber is synonymous with *E. australiana* of Baker and Smith.

The constituents which have so far been identified in the oils from the selection of trees examined between Healesville and Alexandra, Victoria, are *l*-α-phellandrene, piperitone 32–52%, and piperitol. An observation of

TABLE I.

Date.	Locality.	Yield of Oil. %	$d_{15}^{15°}$	$a_D^{20°}$	$n_D^{20°}$	Solubility in Alcohol (by Weight)	Cineol. %	Piperitone. %	Phellandrene.	Remarks.
24.1.35	Crystal Creek 7 miles from Alexandra.	1·35	0·9167	+5·2°	1·4653	1·2 vols. 70%.	50%	—	Absent.	Young foliage aged 4 months. Oil from adult foliage contains 70% cineol.
,,	Between Taggerty and Buxton.	0·53	0·8777	−36·3°	1·4809	6 vols. 80%.	Nil.	—	Abundance.	—
,,	Lilydale.	0·87	0·8713	−64·6°	1·4776	6 vols. 80%.	,,	Nil.	Abundance.	"C."
,,	,,	0·4	0·8882	−65°	1·4812	0·7 vols. 80%.	,,	36	Abundance.	"D."
,,	Healesville.	1·75	0·8748	−48·3°	1·4764	0·8 vol. 80%.	,,	Nil.	Abundance.	"E."
,,	,,	0·95	0·8811	−68·5°	1·4796	3·5 vols. 80%.	,,	32	Abundance.	"F."
15.10.37	Sir Colin MacKenzie's Sanctuary, Healesville.	1·6	0·9036	−50·9°	1·4830	1·4 vols. 70%.	,,	52	Abundance.	—
27.7.33	New Norfolk, Tasmania.	1·18	0·8946	−58·5°	1·4815	0·6 vol. 80%.	,,	18	Abundance.	*E. amygdalina* (Type), included for comparison.

particular interest was made both at Lilydale and at Healesville where adjoining trees were examined. Both sets of trees were botanically identical and yet a slightly different odour could be detected in the foliage of each when crushed between the fingers. A chemical examination of the essential oils confirmed these observations (see " C ", " D ", " E " and " F " in table). Although the trees were growing close together, the essential oil of one at each locality was found to contain 32–36% of piperitone, whilst this constituent was replaced in the respective adjoining trees with piperitol—the corresponding alcohol. Moreover, there was a marked difference in the respective yields of oil, the piperitone-containing oils being obtained in one-half the yield of those containing piperitol.

Through the courtesy of Mr. Ambrose Pratt arrangements were made for a small supply of leaves from the two sanctuaries referred to in his book. The oils obtained from the two lots of leaves received were found to contain phellandrene and piperitone as principal constituents, but no cineol was detected. The oil from the foliage of the tree growing at Sir Colin MacKenzie's Sanctuary at Healesville was found to contain as much as 52% of piperitone, a constituent not previously recorded in quantity in the oil from this species. The botanical material was examined by Mr. E. Cheel, who identified it as *Eucalyptus radiata* (Sieber). This species is synonymous with *E. australiana* (Baker and Smith). Mr. Cheel pointed out that it was not typical of the species but seemed to be intermediate between *E. numerosa* (Maiden) and *E. radiata* of Sieber (not Baker and Smith). The leaf characters differed from typical *E. numerosa*. For the benefit of those unacquainted with the complicated nomenclature of the Eucalypts, *E. numerosa* of Maiden is identical with *E. radiata* of Baker and Smith.

The composition of the essential oil resembles very closely that obtained from *E. radiata* (Baker and Smith), variety A, but a description of the tree supplied by Mr. Pratt, viz. " 50 feet high ; the bark extends right to the top of the tree and along the main branches ", places it beyond doubt as typical *Eucalyptus australiana*. It is evident that a number of physiological forms exist in the Victorian trees of *E. australiana*.

A thorough investigation is now being made of these Victorian trees, using new methods of investigation, but some little time must elapse before the results are available for publication.

ACKNOWLEDGMENTS.

We are indebted to Bosisto & Co. Pty. Ltd., of Melbourne, for the opportunity to carry out the preliminary investigation between Melbourne and Alexandra in January, 1935, and to their manager, Mr. Reilly, for undertaking the distillation of the material collected. Our thanks are also due to Mr. Ambrose Pratt for providing the leaves from the two Koala Sanctuaries in Victoria.

STUDIES ON PHYSIOLOGIC SPECIALIZATION OF THE ORGANISMS CAUSING BUNT IN WHEAT, AND THE GENETICS OF RESISTANCE TO THIS AND CERTAIN OTHER WHEAT DISEASES.

I. Physiologic Specialization Studies.*

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(With three text-figures.)

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Introduction.

Bunt or Stinking Smut of wheat, caused by *Tilletia tritici* (Bjerk.) Winter and *Tilletia levis* Kuhn is world wide in its distribution and importance. Losses are mainly brought about by reduction in yield per acre, and by depreciation in the market value of the grain, which results in dockage being charged.(17) Further, plant growth may be checked, with a consequent reduction in yield(13) (31) even though the usual symptoms are not manifested.

It is estimated that in the United States of America in 1924, an epidemic year, 26 million bushels were destroyed by stinking smut. In that year the loss caused by the disease in Kansas alone was estimated at about 14,811,000 dollars.(24) The average annual reduction during the preceding eight years was 14 million bushels.(39)

Figures relative to losses in Australia are set out elsewhere.(5)

Ordinarily, bunt may be prevented by fungicidal steeps or dusts, but, although copper carbonate and organic

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mercury dusts are effective prophylactics, the procedure is costly.(5) Furthermore, such treatment does not eliminate the disease(38) and is not wholly effective in cases where the inoculum is soil borne. Seed treatment, therefore, must be regarded only as a temporary expedient. The final solution lies in the utilisation of the natural resistance possessed by certain varieties of wheat. Already several commercial wheats have been synthesised, e.g. Florence (Farrer),(8) Ridit and Albit (Gaines).(15) With the appearance of new and more virulent physiologic races, however, these and other varieties hitherto resistant have become infected.(14) New physiologic races may arise by mutation or hybridisation in nature, or they may be introduced from other areas. Physiologic specialization is therefore important in a consideration of the establishment of plant quarantines, in epidemiology studies, and in the production of disease-resistant varieties. Thus, since the problem of breeding for bunt resistance is constantly shifting its ground, not only is a thorough knowledge of the mode of inheritance of resistance a prerequisite to the development of bunt-resistant varieties, but, in addition, it is essential to know something of the physiologic specialization of the fungus.

Gaines and Smith(16) have shown that hybrids of a cross, White Odessa × Hohenheimer, react differently to three physiologic races of bunt. To two races, T_1 and L_4, these varieties have a single factor difference for resistance, but they differ by two factors for resistance when T_{11} is used. This is a very significant fact. The mode of inheritance of resistance within hybrids may change with the introduction or occurrence of new races. Hence it is essential that the plant breeder should know what races of bunt are present, their distribution, their pathogenic capabilities, and the possibilities for the origin and introduction of new races.

The various phases of the work which was commenced in 1930 fall naturally into two divisions. Part 1 deals with the physiologic specialization of the pathogen, recording the occurrence, for the first time in Australia, of three races of *T. tritici* and four of *T. levis*, which were distinguished by pathogenic tests. The results of morphologic studies on the various races are also included. Genetic studies in Part 2, which is to be published later, deal not only with the inheritance of resistance to *T. tritici* but also to *Puccinia graminis tritici* E. and H., and *Urocystis tritici*

Koern., in a wheat cross Federation × Hope. Correlations between these and other characters are estimated and recorded.

REVIEW OF LITERATURE.

Physiologic specialization in the smuts was first clearly demonstrated by Zillig,(43) who showed that *Ustilago violacea* (Pers.) Fcl. comprised several distinct strains which differed in their pathogenicity towards certain host plants.

Rodenhiser and Stakman(32) separated races of *T. levis* in 1927. Since then various workers have demonstrated that physiologic races of *T. tritici* and *T. levis* exist in different countries, but heretofore none have been recorded in Australia. The number of races reported of both species of *Tilletia*, together with the author and date of determination, are given in Table 1.

TABLE 1.

Author, Date of Determination and Number of "Physiologic Races" (Separations) of T. tritici *and* T. levis *determined by Pathogenicity.*

Organism.	Authors and Dates.	Number of "Races".
Tilletia tritici	Rodenhiser,(30) 1928	2
	Reed,(28) 1928	6
	Reichert,(29) 1930	7
	Holton,(18) 1930	3
	Aamodt,(1) 1931	1
	Bressman,(4)	4
	Petit,(27) 1931	1
	Gaines *et al.*,(40) 1932	10
	Feucht,(9) 1932	2
	Brentzel,(3) 1933	1
	Nieves,(26) 1933	6
	Flor,(11) 1933	7
		— 50
Tilletia levis	Rodenhiser and Stakman,(32) 1927 ..	3
	Reed,(28) 1928	4
	Atanasoff D.,(2) 1929	4
	Aamodt,(1) 1931	5
	Holton,(19) 1931..	2
	Bressman,(4) 1931	6
	Petit,(27) 1931	1
	Gaines *et al.*, (40) 1932	12
	Nieves,(26) 1933	2
	Flor,(11) 1933	6
	Melchers,(25) 1934	7
		— 52

The use of the term "physiologic races" is not strictly correct. Here it refers to bunt collections which have been separated by several authors on pathogenic differences. A single collection may contain several physiologic races. Furthermore, as no standard set of differentials was used in the determination of the 102 "physiologic races" it is not known how many distinct strains are actually represented by these collections.

MATERIALS AND METHODS.

In the summer of 1931 collections of bunt were made from all the important wheat-growing areas in Australia, and the geographic distribution and prevalence of the two species of *Tilletia* determined.(6) As the result of preliminary tests, sixteen of these were selected from widely separated centres and were used in the studies.

(a) Tests of Pathogenicity.

In order to compare the virulence of Australian collections of bunt with other known races, eleven varieties of wheat, which were sown in the spring of 1932 at the University Farm, St. Paul, Minnesota, U.S.A., were also inoculated with the Australian collections and with three races of *T. tritici* and three of *T. levis* already determined by Reed.(28) The species, number, and sources of the sixteen collections are listed in Table 2.

TABLE 2.

The Species, Sources, and Numbers of the 16 Collections used in the Physiologic Specialization Trials.

Species.	Number.	Source.
Tilletia tritici.	N.S.W. 1	Dr. W. L. Waterhouse, Sydney, N.S.W., Australia.
	T. 2	Dr. G. M. Reed, U.S.A.
	N.S.W. 2	Wagga, N.S.W., Australia.
	N.S.W. 14	Lake Cargelligo, N.S.W., Australia.
	S.A. 5	Port Neill, South Australia.
	Aby.	Aberystwyth, Wales.
	T. 9	G. M. Reed, U.S.A.
	T. 1	G. M. Reed, U.S.A.
Tilletia levis.	N.S.W. 5	Tamworth, N.S.W., Australia.
	L. 5	G. M. Reed, U.S.A.
	L. 10	G. M. Reed, U.S.A.
	N.S.W. 8	Tooraweenah, N.S.W., Australia.
	L. 1	G. M. Reed, U.S.A.
	N.S.W. 9	Cumnock, N.S.W., Australia.
	W.A. 39	Dowerin, Western Australia.
	S.A. 19	Pinaroo, South Australia.

The quantities of grain and inoculum used in each case were the same. They were shaken together in a glass tube until the grain was thoroughly blackened, thus ensuring a maximum spore load. All varieties were sown two inches deep, in rows one foot apart. Sowing was done on the same day in order to eliminate as far as possible the effects of changing environmental conditions. Germination tests showed that the spores in all collections were equally viable.

(b) Biometrical Studies.

Representative samples of spores were taken from each collection in 1931, 1933 and 1934 and the size determined by measuring the greatest diameter of each of 400 different spores, selected at random; the figures thus obtained were used to calculate the mathematical constants.

TABLE 3.

Percentage of Bunt Infection in Certain Wheat Varieties Inoculated with Collections of Bunt and Grown at St. Paul, Minnesota, U.S.A., in 1932.

Collection of Bunt.		Differential Variety.			
		Kota.	Progress.	Preston.	Red Bobs.
			Tilletia tritici.		
N.S.W.	1	52·9±1·83	24·7±2·01	2·4±0·78	27·2±1·55
T.	2	44·9±2·44	31·4±2·11	0·6±0·29	24·6±0·99
N.S.W.	2	41·7±2·43	3·1±0·26	0	
N.S.W.	14	33·6±2·25	14·5±1·23	1·7±0·85	6·8±0·80
S.A.	5	46·0±1·94	10·1±1·50	4·7±1·24	5·6±0·48
Aby.		0	34·3±1·01	5·9±0·68	1·6±0·35
T.	9	0·6±0·26	30·3±0·98	3·1±0·82	1·4±0·23
T.	1	57·0±1·48	14·4±1·10	5·7±0·24	24·3±1·23
			Tilletia levis.		
N.S.W.	5	5·8±0·24	13·2±0·94	3·9±0·24	30·7±1·24
L.	5	58·5±1·34	19·9±0·93	5·9±0·32	28·2±0·98
L.	10	48·5±1·01	32·1±0·84	5·2±0·43	26·4±1·03
N.S.W.	8	11·3±0·98	0	0	0·5±0·26
L.	1	52·9±1·02	22·1±0·57	7·9±0·42	16·6±0·77
N.S.W.	9	33·2±0·76	19·5±1·33	1·7±0·21	1·5±0·16
W.A.	39	38·4±0·98	12·3±0·74	10·6±0·53	17·9±0·73
S.A.	19	12·6±0·93	6·0±1·34	0	0
Check		0	0	0	0

Precautions were taken to ensure uniformity of conditions of measurements, a calibrated Zeiss microscope with constant illumination from an artificial source of light being used for the work. The spores were dusted on to slides smeared with albumen, and a 50 per cent. aqueous solution of lactic acid was used as the mounting medium.

EXPERIMENTAL RESULTS.

Pathogenicity.

Four of the wheats, viz. Kota, Progress, Preston, Red Bobs, acted as differentials, and to a lesser extent Emmer also served this purpose.

The infection percentage was calculated by head counts in the row, approximately 200 heads being counted. Table 3 shows the percentage infection obtained, which is the average of three replications in randomised blocks.

TABLE 4.

Percentage of Bunt Infection in Certain Wheat Varieties Inoculated with Collections of Bunt and Grown at Richmond, N.S. Wales, in 1933.

Collections of Bunt.	Differential Varieties.			
	Kota.	Progress.	Preston.	Red Bobs.
		Tilletia tritici.		
N.S.W. 1	52·5	25·5	9·6	30·6
T. 2	76·7	47·3	39·4.	38·0
N.S.W. 2	55·6	18·6	8·8	7·5
N.S.W. 14	64·0	66·7	53·3	68·3
S.A. 5	53·8	17·1	11·1	6·2
Aby.	13·6	57·8	20·0	14·9
T. 9	17·8	44·3	32·3	19·6
T. 1	56·5	68·2	28·5	35·5
		Tilletia levis.		
N.S.W. 5	13·1	32·7	16·8	34·9
L. 5	61·0	10·0	0·0	36·7
L. 10	100·0	62·5	27·3	53·3
N.S.W. 8	30·2	10·2	18·2	18·4
L. 1	74·0	41·7	29·4	38·1
N.S.W. 9	81·6	52·3	27·4	8·9
W.A. 39	78·0	50·2	41·2	70·0
S.A. 19	57·5	35·5	18·2	18·5
Check	0·0	0·0	0·0	0·0

As a result of the indications of specialization in *Tilletia* in the preliminary tests in 1932, the four differential varieties were inoculated with the sixteen collections and sown at the Hawkesbury Agricultural College, Richmond, N.S. Wales, in 1933. The same methods were employed as in 1932. The percentage of infection obtained in 1933 for each variety is recorded in Table 4.

The amount of infection obtained in both years in four varieties of wheat inoculated with sixteen collections of bunt is represented in Figs. I and II.

In addition to the races already described by Reed, there appears to be three races of *T. tritici* in the Australian collections listed above:

Race 1 is distinguished by its ability to infect Kota, Progress and Red Bobs—the former most heavily. It is represented by collection N.S.W. 1 and produces a reaction similar to form T_2 of Reed's collection in 1932. However, in 1933 Preston was attacked by T_2. A similar happening with T_1 is commented upon later.

Race 2 is characterised by infecting only Kota; N.S.W. 2 and probably S.A. 5 are included here.

Race 3 attacks Kota and to some extent Progress. It includes collections N.S.W. 14. Although Red Bobs was attacked in 1933, the race still remains distinct from the preceding two, and like Race 2 does not correspond to any of the races determined by Reed.

The collection from Aberystwyth gave similar results to T_9. This is not surprising, as both collections came from Britain. In 1933 race T_1 severely attacked Progress; this was unexpected, as was also the heavy infection of Red Bobs by Race 3. At present no explanation of this happening is offered, unless it be that the collection contained a mixture of races. Experiments are being conducted to test this supposition.

There appear to be four races of *T. levis* present in the collections examined. Reed has not described any corresponding races.

Race 1 is characterised by infecting Red Bobs, and, to a lesser extent, Progress. It includes collection N.S.W. 5.

Race 2 is weakly parasitic on Kota and includes collection N.S.W. 8.

Race 3 infects Kota and to a lesser extent Red Bobs and Progress. Collection W.A. 39 is included here.

Race 4 resembles Race 3 in attacking Kota and to a lesser extent Progress, but does not infect Red Bobs. It includes collections S.A. 19 and N.S.W. 9.

Biometrical Studies.

Although the criteria for determining races of the fungi are primarily physiological, small but significant morphological differences sometimes may be used as a means of separation.

In studies of comparative morphology of the cereal rusts, Levine(22) showed that the urediospores of several physiologic races of *Puccinia graminis tritici* differed significantly in size. Waterhouse(42) working with naturally occurring Australian races of several cereal rusts, demonstrated similar dimensional differences. Several workers(3) (20) (34) have shown that a number of physiologic races of *T. tritici* differ in size and shape of bunt balls.

Representative samples of the sixteen collections were taken in 1931, 1933 and 1934 and examined for size of spores as well as for the size, shape and consistency of the bunt ball. Table 5 shows the distribution of individuals in 1μ classes for spore size. The numbers in each class are the sum of the frequencies for 1931, 1933, 1934. They are grouped because there was no significant difference between the mean spore sizes in each of the collections during the three years. In fact the consistency of the results for the different years is noteworthy and indicates that seasonal conditions do not materially influence spore size. For example, the mean sizes of collection N_1 in 1931, 1933, and 1934 were respectively $18{\cdot}10\mu \pm 1{\cdot}04$, $18{\cdot}11\mu \pm 1{\cdot}02$, and $18{\cdot}00\mu \pm 1{\cdot}03$.

In the collections under observation, the spores were generally spherical in shape, although a few, especially in *T. levis*, because of lateral compression became elliptical or more or less cubical. It will be observed that, contrary to expectation, the distribution of individuals about the mean does not conform to a normal curve of error ; there appears to be a dearth of numbers at the minus end of the distribution. It should be remembered, however, that as measurements were made on the greatest diameter of the spore, all those abnormally shaped gave figures greater than

Fig. 1.—Relative bunt infection in four varieties of wheat inoculated with collections of *Tilletia tritici*.

Fig. 2.—Relative bunt infection in four varieties of wheat inoculated with collections of *Tilletia levis.*

TABLE 5.

Means and Frequency Distribution in 1μ Classes for Spore Size of Collections of T. tritici *and* T. levis *for 1931, 1933 and 1934.*

Collection	13	14	15	16	17	18	19	20	21	22	23	24	25	Total.	Mean.
T. tritici—															
T_1			9	127	353	436	195	69	6	5				1200	17·78 ± 1·11
T_2			1	75	337	431	228	117	11					1200	18·00 ± 1·10
T_9			5	117	398	445	158	70	7					1200	17·73 ± 1·05
Aby			5	46	238	461	249	184	17					1200	18·27 ± 1·13
N_1			10	49	269	514	240	116	2					1200	18·07 ± 1·03
N_{14}				71	327	433	217	109	22	13	5	3		1200	18·11 ± 1·19
S.A.$_5$			5	79	297	449	262	91	17					1200	18·02 ± 1·09
N_2				10	30	66	265	523	199	58	38	11		1200	19·96 ± 1·26
T. levis—															
L_1	3	54	129	519	196	121	83	68	18	5		4		1200	16·72 ± 1·62
L_5	4	17	67	576	226	142	87	64	16	1				1200	16·83 ± 1·40
L_{10}	1	9	60	586	233	183	67	44	14	3				1200	16·82 ± 1·30
N_8		5	56	548	305	141	84	61						1200	16·84 ± 1·23
N_9		14	79	533	244	155	99	76						1200	16·87 ± 1·35
N_5		23	68	557	243	119	70	100	20					1200	16·89 ± 1·48
W.A.$_{39}$	2	15	27	430	291	212	117	80	23			3		1200	17·21 ± 1·47
S.A.$_{19}$			5	133	214	275	345	141	50	25	2	7	3	1200	18·38 ± 1·53

normal individuals of the same size. Consequently the numbers at the plus end of the distribution were in excess of those expected, which resulted in the formation of a skew curve.

The mean size of the spores of *T. tritici*, which was calculated by taking the figures of all collections in the three years, is 18·24μ±1·12, with a range of 15–24, while that of *T. levis* is 17·07μ±1·49, with a range of 13–25. The difference of 1·173μ±1·86 is not significant. In the collections examined, the ranges in both species are approximately the same as those given by McAlpine,(23) and, although the mean spore size of *T. tritici* appeared to be greater than that of *T. levis*, a significant difference could not be established.

A comparison was made of all the collections in each species, but no significant difference in the mean spore size was obtained.

The size, shape, and consistency of the bunt balls from the various collections showed no real differences. Although all grades of consistency from hard and stony balls to dry and powdery, or soft and greasy samples were found, none remained a constant characteristic of any one collection in the inoculation experiments carried out during the three years.

The same is true for the shape of the bunt balls of collections which were selected and grown on varieties of wheat with different shaped kernels. It was found by cross inoculation that the bunt ball of any collection assumes the shape of the kernel of the host plant, although seasonal conditions may cause slight modifications.

PATHOGENICITY TESTS IN 1935–36.*

In the results of the work on physiologic specialization in bunt which were carried out in 1931–34 at least two questions were suggested as worthy of further investigation. It would be desirable to know, firstly, how many of the seven races, established from the Australian collection, correspond with those already determined in other parts of the world, and secondly, how constant are the reactions of the selected differential varieties to the races of bunt.

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* Financial assistance, which is gratefully acknowledged, has been received from the Science and Industry Endowment Fund and the Carnegie Research Fund for the continuance of the work.

With a view to answering these, and other questions, the four differential varieties of wheat were inoculated with the races used in 1931–34, and, in addition, with a number of known races of bunt.

The source, number, and designation of the additional races of *Tilletia tritici* and *T. levis* are shown in Table 6.

TABLE 6.

Source, Number and Designation of 72 additional Collections of Bunt used in Physiologic Specialization Trials, 1935-36.

Source.		Number of Races.	
		T. tritici.	*T. levis.*
O. S. Aamodt, Alberta, Canada.	Al.	1	5
Dominion Rust Research Labs., Manitoba..	Man.	1	1
E. F. Gaines, Pullman, Wash., U.S.A.	Ft, Pt, Fl, Pl	7	8
E. N. Bressman, Oregon, U.S.A.	Or.	32	16
I. Reichert, Palestine	R.	1	0

The grain was inoculated and sown at the Hawkesbury Agricultural College, Richmond, N.S.W., in 1935 and 1936, employing the same technique as in previous years.

Results.

The percentage of infection generally was greater in 1936 than in 1935. In these years the reactions of the differentials were similar to those obtained with the same races which were used in the 1931–34 tests, with three exceptions. In 1935 Preston was not attacked by T_2 or N_{14}, but in 1936 it was heavily infected by these races. Similarly, Progress, which was attacked by T_1 in 1936, showed a relatively small percentage of bunted heads in 1935. In the case of the seventy-two collections which were tested only in 1935–36, forty-one gave constant reactions in replicated rows during the two years, whilst the remaining thirty-one were variable.

The forty-one collections could be arranged in eleven groups according to the reactions of the four differential varieties, viz. Kota, Progress, Preston, Red Bobs. These types of reaction may be represented diagrammatically as in Fig. 3.

In type 1 Kota is moderately susceptible and Preston resistant, whilst Red Bobs and Progress are fully susceptible ; type 2 is characterised by the great susceptibility of Progress, the moderate susceptibility of Preston and Kota, and resistance of Red Bobs ; and so on.

Of the races which were established in 1931–34, N_5, Aby, N_9, N_{14}, T_2 and W.A.$_{39}$ give reactions similar to types 1, 3, 4, 6, 7, and 9 respectively, i.e. four of the Australian races correspond to others which have been described.

The collections which give the various types of reactions with the differentials may be grouped as follows :

Type 1 Pt_2, Or_{22}, Or_{33}, Or_{42}.
,, 2 Al_2, Pl_5, Pt_3, Pt_4, Ft_4, Or_{10}, Or_{15}, Or_{35}, Or_{40}.
,, 3 Fl_1, Pt_1, Ft_6, Or_{18}, Or_{32}, Or_8.
,, 4 Or_4, Or_{24}, Or_{31}, Or_{40}.
,, 5 Or_5, Or_{14}, Or_{21}, Or_9.
,, 6 Man_1, Man_2, Or_{48}.
,, 7 Or_{11}, Or_{12}.
,, 8 Or_{13}, Or_{23}, Or_{39}.
,, 9 Or_{31}, Or_{44}, Fl_3.
,, 10 Or_{38}.
,, 11 Or_{25}, Or_{26}.

The four differentials gave relatively constant reactions to most of the collections that were used. It would seem reasonable, then, to suppose that, under Australian conditions, there are some races of stinking smut which may be expected to maintain a constant pathogenicity in nature. On the other hand, there are some collections which are very variable. This, as shown previously, is not surprising when the life history of the organism is considered.

The behaviour of Preston to two of the races is interesting. This variety was resistant to races T_2 and N_{14} under the conditions which prevailed in 1932 and 1935, but in 1933 and 1936 it was susceptible. This, again, is not surprising, because, as shown previously, resistance can vary only within the limits set by the genes. So that to certain races and under set conditions Preston behaves as a differential, whilst under other conditions the reverse is true.

Furthermore, these four varieties, which differentiated between some of the seventy-two races, did not act as

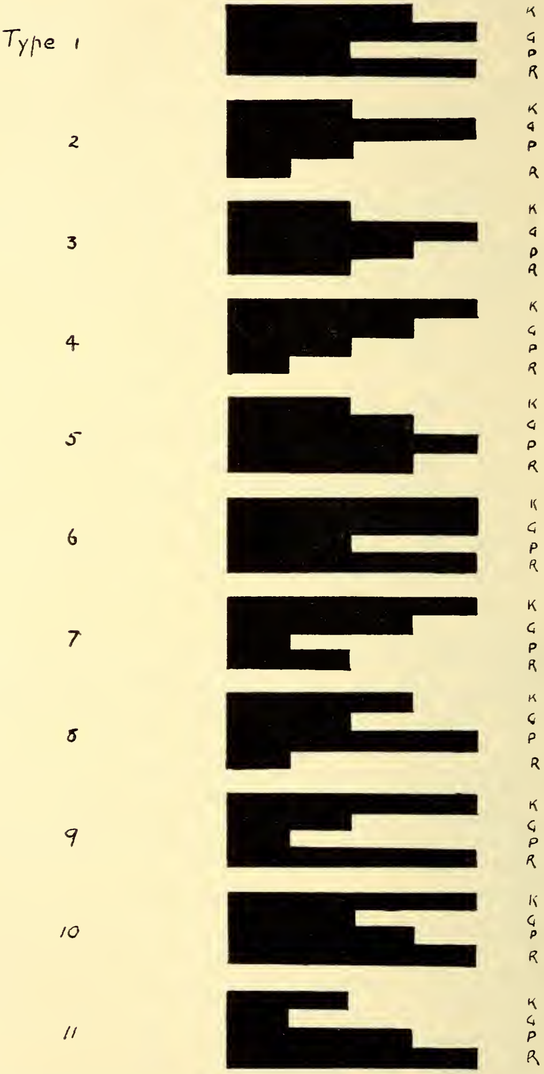

Fig. 3.—Types of reaction of four differential varieties: Kota (K), Progress (G), Preston (P), and Red Bobs (R), to collections of bunt in 1935-36.

differentials to others under Australian conditions, e.g. four races from Oregon all gave the reaction of Type 5.

For practical plant breeding purposes, then, it would seem desirable that the determination of races within the species of *Tilletia* should be carried out in the particular region where the host plant is to be grown, and with varieties which will act as differentials in that area.

Discussion.

The concept of physiologic specialization has broadened since the time when the " Gewohnheitrassen " of Magnus and the " biologische Rassen " of Rostrup were separated by their infective capacities. Stakman(35) has pointed out that within species there are races which may differ in one or more characteristics. Thus not only may they be distinguished by their ability to infect certain host varieties, but also by their characteristics when cultivated on artificial media, by physiologic and ecologic relations, by physico-chemical tests and to a lesser extent by their morphology.

It is not surprising to find that pathogenic tests are the chief means of differentiating races, for breeders and growers are concerned mostly with the effects of races of the pathogen upon the crop. Differences in cultural growth of *Tilletia* spp. have been determined by Kienholz and Heald,(21) Flor,(12) and Melchers.(25) However, Flor(12) has pointed out that these should not be used as criteria, because the haploid nature of the mycelial growth is different from the diploid condition in the propagative and infective phase. During three years the writer was unable to establish any consistent differences on growth on artificial media, using all the collections set out in Table 1.

It does not seem likely that the inconsistent results obtained in a study of the size, shape and consistency of the bunt balls were due to admixture of races in each collection. It is considered that the shape and consistency of the bunt balls are determined more by morphologic characters of the host and the season than by any inherent characteristics of the pathogen.

Apart from the fundamental questions which arise from a consideration of physiologic specialization in the smuts, there are certain important implications in the practical phases of plant pathology.

The appearance of new races may be due to mutation, hybridisation, or introduction. Hence a knowledge of specialization is necessary in order to understand more clearly the causes of epidemics and the infection which suddenly appears in varieties hitherto classed as resistant. Further, the enactment of plant quarantine legislation against the possible introduction of additional races is important.

Physiologic specialization may offer an explanation of the sudden appearance of disease in epidemic proportions. Under favourable environmental conditions resistant varieties may succumb to new and more virulent races of pathogen.

In 1925, the Durum wheats, which were introduced into North and South Dakota on account of drought and disease resistance, showed an alarming increase in the amount of bunt present in the crops. It was shown(19) that the existence of one or more new physiologic races of *T. tritici*, hitherto not present or widely spread, was responsible for this epidemic.

Prior to 1930, Marquis, a hard red American spring wheat, was considered highly resistant to bunt. In that year, fields of this variety in Minnesota were reported with approximately 40–50 per cent. infection. Subsequent trials revealed that a new race of *T. levis* was the cause of the heavy infection.(19) These and numbers of other examples illustrate how the occurrence of new races may be an important factor in the development of epidemics, and therefore a thorough knowledge and understanding of the meaning of physiologic specialization is essential for a proper interpretation of epidemiology.

Information regarding the physiologic specialization of plant pathogens is fundamental to any sound plant quarantine legislation, for the number and virulence of the strains of fungi is not necessarily the same in every country. Reed(28) has shown that collections of smut from several countries vary in their virulence towards certain hosts.

Further, Rodenhiser and Stakman(32) tested the pathogenicity of *T. levis* collections from Hungary, Minnesota, and Egypt, and *T. tritici* collections from Norway and New Zealand on certain varieties of wheat. Each collection proved to be a distinct physiologic race.

It has been shown that four of the Australian races correspond in their infective capacity with those already determined in other places.

Quarantine measures, then, may be desirable to prevent the entry of new or more virulent physiologic races—even though the pathogen be present in the country.

In developing smut-resistant varieties of cereals it is necessary to consider the geographic distribution, number, pathogenic capabilities, and the degree of constancy of the physiologic races of the pathogen.

A variety may be resistant in one locality and yet very susceptible in another.(19) It is therefore desirable to know the reaction of the prospective variety to all known races of smut in the district in which it is to be grown.

Varieties of cereals are known to differ in their reaction to the smuts,(37) and disease-resistant varieties, which incorporate desirable agronomic characteristics, have been synthesised.(14) Some of these lines have suddenly become susceptible to disease and the question arises whether these " resistant " varieties retain their resistance permanently. Dillon-Weston(7) claims to have " broken down " the resistance of some varieties of wheat to bunt by using inoculum obtained from the parent plant in the previous season. His results may be explained by a screening effect brought about by culturing bunt on certain varieties of wheat.

The matter of breeding disease-resistant varieties is made more difficult by the fact that the reaction of certain varieties to a given physiologic race of bunt may differ with varying environmental conditions. Smith,(33) for example, has pointed out that Hope wheat, when spring sown in Washington, is resistant to several races of bunt, but becomes moderately susceptible when fall sown. It is, therefore, not only necessary to know whether one race is more virulent than another but also to be acquainted with the reaction of a host variety to that race under varying conditions. Resistance varies within a set of limits which are determined by the interaction of the environment and the genetic constitution of the host. The problem, therefore, becomes one of determining the range of variability due to environment. This point cannot be emphasised too strongly, for each situation which arises demands a consideration of the host, the pathogen, and the interaction between the two. Further, because of the very nature of the variable environment, the relationship must be considered over a large space and a long period of time.

The " modus vivendi " of the smuts further complicates the problem. It is generally believed that, under given conditions, the resistance of a variety to a disease remains constant, so that changes in infection, apart from minor fluctuation due to environment, must be brought about by a change in the pathogenic capability of the disease-causing organism. Hybridisation in the fungi, which occurs in nature (and this holds true for rusts as well as the smuts), may account for such a change.(11) In the rusts, æciospores, the primary infection spores of cereals, can develop only when two compatible nuclei become associated. Likewise no infection usually takes place in the smuts without the association of compatible nuclei derived from different sporidia. However, the rusts have a repeating urediospore capable of living over from year to year in the presence of suitable host plants and again causing infection. This is particularly true under the conditions existing in the wheat growing areas of Australia. In this spore the nuclei are associated dikaryotically and therefore while in this condition maintain a constant pathogenicity.

On the other hand, it would seem that the pathogenicity of a given smut collection could change from time to time due to sexual fusions often between haplonts with different factors for pathogenicity, which results in new and more virulent strains due to a recombination or accumulation of factors.

It is probable, however, that varieties exert a selective influence in screening out the less virulent smut combinations, tending to build up homozygous strains.

Gaines maintained the purity of race T_2 by culturing it for a number of years on Hussar, a variety which is susceptible only to this race of *T. tritici*. The method was also used for " varietal screening " by Flor,(12) who successfully separated *T. tritici* and *T. levis* from a mixture by making use of their differential infective capacities on Oro and Albit or Hussar, The limitations and the possibilities of separating physiologic races by these means can be demonstrated only by results of experiments extending over a number of years.

Physiologic races in the smuts which are chlamydospore collections from different geographic areas and which give relatively constant pathologic effects on certain hosts, may, then, contain several haploid and dikaryotic biotypes.

One hundred and two of the races which have been determined elsewhere already, can be grouped into eleven types according to their infective capacities when grown under Australian conditions. Four of the Australian races were similar in their reaction to a corresponding number of these types. While this simplifies the position in some degree, it does not answer many of the questions concerned with present status of the physiologic specialization in the bunts.

Much confusion may arise from a comparison of results from institutions where the work is carried out under different conditions of light, temperature, moisture, etc., and this difficulty will be overcome only when a determinative technique is standardised.

In cereal rust work a standard set of differentials is used but the conditions under which they are cultured are not the same in different parts of the world. Some races are known to give reactions which vary from resistance to susceptibility with a range of 10–12 degrees F. Waterhouse(41) has pointed out that new races may be determined erroneously under these conditions.

How much more confusing, then, is the position in the smuts, where neither differentials nor environmental conditions are standardised. From a systematic standpoint, it may be desirable to establish a central bureau where workers throughout the world may send their collections for determination. Here the adoption of a standardised determinative technique will solve many of the problems. On the other hand one important phase of the problem is purely practical and it would seem advisable, then, that the determination should be carried out in the regions where the results are to be applied.

SUMMARY.

1. Bunt or stinking smut of wheat caused by *T. tritici* and *T. levis* is world wide in its distribution and importance.
2. The present prophylactic methods, although effective, are costly and ultimately must be replaced by the use of resistant varieties. A knowledge of the physiologic specialization of the pathogen is a prerequisite to a sound plant breeding programme.
3. Collections from widely separated centres in all the Australian wheat-growing areas were tested during three years for the presence of physiologic races.
4. Three races of *T. tritici* and four of *T. levis* were demonstrated for the first time in Australia by pathogenic tests.

5. There was no difference in the size of the chlamydospores of the collections of *Tilletia tritici* and *T. levis*.

6. No differences were demonstrated in size, shape, or consistency of bunt balls, or in cultural growth on artificial media of the different races.

7. The investigations were continued in 1935 and 1936 using a large number of races. The additional results indicated that some collections maintain a constant pathogenicity over a number of years, whilst others vary in this respect. A number of races from foreign collections were grouped under eleven types according to the reaction of four differential varieties. Four of the known Australian races correspond with others determined elsewhere.

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ON SOME MAJOR GEOLOGICAL FAULTS NORTH OF RAYMOND TERRACE AND THEIR RELATION TO THE STRUCTURE OF THE STROUD-GLOUCESTER TROUGH.

By G. D. Osborne, D.Sc.

(With Plate III.)

(*Manuscript received, November 17, 1937. Read, December 1, 1937.*)

Introductory.

Since 1927 the writer has been engaged in intermittent field studies connected with a regional survey of the structural geology of a large province in the northern part of the State of New South Wales. This region embraces the Upper Hunter, Upper Manning, and part of the Middle Hastings Valleys, as well as the whole of the northern and eastern side of the Middle and Lower Hunter Valley. In addition, the Stroud-Gloucester Trough and the country immediately east of it have been included. The total area of all these districts is approximately 6,000 square miles.

Altogether, about fourteen months have been spent in field work, and a very considerable quantity of information has been accumulated. It has been the aim of the writer to endeavour to survey the significant structures, and to trace the structural evolution of the areas, with the special purpose of obtaining as much information as possible concerning the late-Palæozoic diastrophism which has affected the province. Evidence concerning other epochs of crustal activity has also been examined. Various districts have been selected as "key" localities and a fairly detailed study has already been made of a number of these. The areas and geological units that have been the subject of detailed study include the following:

The Murrurundi-Isis River district.
The Scone-Gundy syncline.
The Timor anticline.
The Moonan syncline and the Beltrees dome.
The Rouchel Basin.

The Tomalla-Pigna Barney region.
The Rawdon Vale-Gloucester district.
The Clarencetown-Thalaba-Dungog area.
The northern side of the Mirrannie Basin.
The southern end of the Stroud-Gloucester Trough.
The Upper Paterson, Upper Williams and Barrington Tops areas.
The Yarras-Comboyne district.
The Barry-Glenrock-Ellerston region.

Many broad structures have been mapped and detailed work has been done where necessary. Much yet remains to be done, but some striking results are to hand. The fault-patterns and the trends of the folds give many data of outstanding interest concerning the probable relations of the various diastrophic movements which have affected the region. It is proposed to deal with the whole problem in a series of papers now in preparation. The present note is one of several preliminary communications and refers to the problem of the early phase of the late Palæozoic movements. Some aspects of this subject were partially dealt with by the writer in former papers (Osborne, 1921 and 1929).

Field work in 1932, 1933, and during the present year included the mapping of the continuations of certain of the faults described in 1922, and, in particular, led to a recognition of the relations between the Tarean and Williams River Faults and the southern end of the Stroud-Gloucester trough, which it is the purpose of the present paper to discuss briefly.

General Structural Features: The Tarean Fault.

The accompanying map shows the structural relations of the south end of the Stroud-Gloucester trough and the Clarencetown-Raymond Terrace district. The boundaries of the various series along the trough, as shown on the map, are only approximately drawn, as it was found difficult in places to delineate the junctions between the different series.

The remarkable Stroud-Gloucester trough, which is developed in Upper Palæozoic rocks, has been known to geologists for a long time, but no systematic work upon the structure as a whole has yet been made, the only detailed work upon it being that of C. A. Sussmilch (1921), who dealt with the Gloucester or northern end of the trough and pointed out that there the structure is that of a simple syncline developed in Carboniferous and Permian rocks, which have suffered a considerable amount of faulting.

The writer spent several weeks in field work upon various parts of the trough, and in 1933 was struck with the following features of the basin :

(*a*) The noticeable swing in the strike between Booral and Stroud. This is in contrast with the almost constant meridional strike elsewhere.
(*b*) The warping of the base of the trough and its effect on the course of sedimentation in Kamilaroi times.
(*c*) The prevalence of faulting in the central zones of the trough.
(*d*) The interesting genetic relations of certain large faults with the basin, and particularly with the migration of the axis of the trough during its growth.

Other abundant evidence of the Kamilaroi rocks having been affected by steep normal faulting may be seen in a zone a little west of the main axis of the syncline. The coal measures are often thrown into almost vertical positions, as may be noted in the Craven, Mammie Johnson Creek, Ward's River and Weistmantels districts.

A study of the dips and a knowledge of the stratigraphy of the Kuttung Series as exposed between Raymond Terrace and Booral have definitely established the existence of a fault which was suggested by Professor David (1907, p. 56) as cutting through the Stockton-Limeburner's Creek Basin. This has now been named the Tarean Fault. Its effects are best seen in the dislocation and offsetting of the lavas and glacial beds of the Upper Kuttung, but the evidence of the northern continuation of this fault from the region mapped by David may be summarised as follows :

(*a*) The erratic behaviour of the strata in a zone a little to the west of the North Coast Road between Booral and Cromarty Creek (see map).
(*b*) The displacement of the Kuttung units.
(*c*) The shattering of the rocks and the development of tensional joints which dip steeply to the west.
(*d*) The inclined axial plane of the syncline and the local steepening of the eastern limb of the fold on a line in continuation of the fault zone.

North of the limit of the Tarean Fault (as traced so far) the strike of the synclinal axis makes a notable departure from the meridian, and actually trends north-west for eight miles between Booral and Stroud. This is associated with a definite asymmetry of the basin, and it is considered that this exceptional westward bulge of the trough is the result of a continuation in this district of the compression (which produced the fold) when the more northerly and more southerly sections of the basin suffered collapse and fractured, particularly within the central tracts. It is hoped that confirmation of this view will be forthcoming from the more detailed examination of the trough yet to be made.

Thus, from the brief statement above it is seen that the Tarean and other faults in the basin were closely related to the growth of the basin, and occurred in regions of tension flanking the Booral-Stroud zone where compression was acting simultaneously.

THE WILLIAMS RIVER FAULT.

The Williams River Fault was mapped after being traced in 1921 from Raymond Terrace through the Kuttung province to east of Clarencetown (Osborne, 1922). Its presence along the Lower Williams River was recognised by Professor David (1907, p. 65), but its northward extension was at that time not known. Recent work has made possible the tracing of the fault still further to the north, and the throw appears to be increasing in that direction.

The full effect of the heavy throw of the fault is appreciated by an examination of the section near Nooroo. As shown on the map the Burindi rocks (typical of the Hilldale facies) form a belt which has its origin in the duplication of the Dungog-Wiragulla Burindi belt. East of the Nooroo Burindi outcrops, the Kuttung rocks again succeed and the hornblende andesite, acting as an indicator of the repetition of the Volcanic Stage, is seen crossing the Stroud road. These rocks form the western side of the trough here.

The Williams River Fault has a fairly steep dip and possesses a certain amount of "swinging" in the strike (see map). It is a true strike fault in the northern part of the field, and eventually becomes a dip fault when it intersects the curving nose of the plunging Williams River anticline. The result of its position in this pitching anticline causes the eventual disappearance from surface outcrop of the Burindi rocks so well developed at Nooroo.

The placing in juxtaposition of the Kuttung and Burindi Series is a feature of this fault. The most notable effects are seen east and south-east of Dungog. As shown by Sussmilch (Sussmilch and David, 1919), the Wallarobba or Basal Stage conglomerates outcrop on the eastern side of the Dungog Railway Tunnel, while the western portal of the tunnel exposes typical Upper Burindi mudstone. The actual junction of the two series was determined by the writer in 1933, and can be seen very clearly on the roadside a little to the north of the tunnel. Further east, approximately two miles from the outcrop of the base of the Kuttung Series, the hornblende andesite (Martin's Creek type), crops out and can be traced to the south intermittently through the Volcanic Stage province until it is found eventually near Clarencetown on the east side of the Williams River. Between the outcrop on the Nooroo Road and its occurrence near Clarencetown the lava is the basal unit in a series of Volcanic Stage rocks outcropping in the Thalaba-Three Brothers district. These rocks owe their present position to the Williams River Fault.

Now the map shows the evidence for the intimate connection between the fault and the western margin of the Stroud trough. The fault parallels the trend of the western side of the basin and clearly was developed in the same period of earth movement. In fact, in addition to running parallel to the axis of the trough, even to the point of some correspondence in strike where the axis of the trough departs from the meridian, the fault is found breaking through the weak summit of the anticline which is the complementary structure to the Stroud trough at its southern end.

The recognition of this relationship is of special interest in connection with the age of the fracture, because, as shown on the map, the Williams River Fault when followed south does not appear to displace Upper Coal Measures south of Raymond Terrace. In this particular its behaviour is precisely similar to that of the Butterwick Fault, and certain others of the Paterson-Seaham area (see map). It is barely possible that all these strong faults die out before reaching the outcrops of the Upper Coal Measures, and even at the very junction of the Upper Marine Series and Upper Coal Measures. Rather we have in the features seen south of the Kuttung province good evidence of the strong faults, such as the Williams River Fault, having been formed in association with folding, and in pre-Newcastle time. The probable epi-Upper Marine age for a considerable portion of the Late Palæozoic earth movements has been pointed out before (Osborne, 1929, p. 449) and this view is shared by most, if not all, geologists who know the Hunter region well. Thus it is to be stressed that the relationship of the Williams River Fault and the Stroud-Gloucester trough, as now known, strengthens the view expressed by the writer (see 1929, p. 460) that the Stroud-Gloucester Basin was of quite early development in the evolution of the Late Palæozoic structures. Its compression, in part, antedated the formation of the Upper Coal Measures, but how much modification of the pre-Coal Measure fold occurred at a later period is a problem almost incapable of solution on the present evidence. One important result of our enquiry now emerges, viz. that the Williams River Fault is older than the Tarean Fault, the latter being one of the fractures that developed in that part of the late Palæozoic diastrophism which was epi-Newcastle in age.

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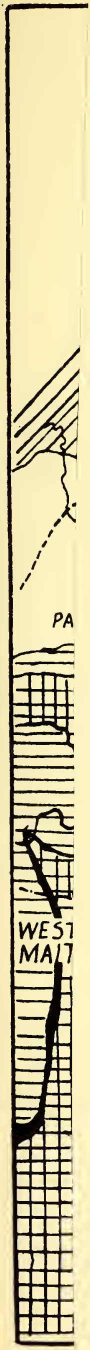
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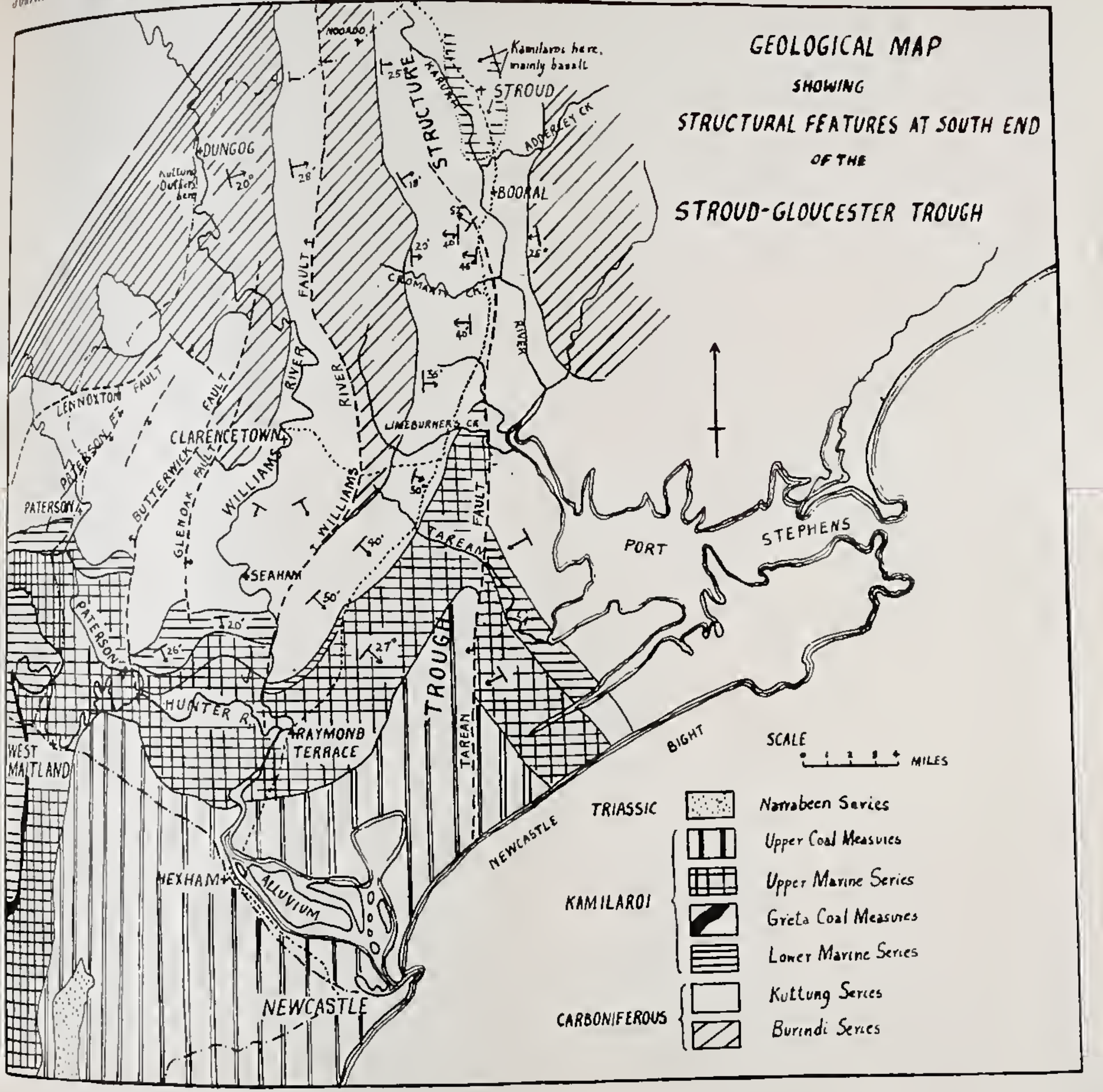

THE CONSTITUTION OF GMELINOL.

PART I.

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H. G. Smith (*Proc. Roy. Soc. N.S.W.*, 1912, *46*, 187) reported the isolation of a crystalline substance from the wood of *Gmelina Leichhardtii*, the "Colonial Beech". Smith seems to have isolated the material used for his investigations from "shakes" in the timber which had become filled with crystalline material, but this method is obviously not suitable for obtaining the material in sufficient quantities for an exhaustive investigation, being dependent on the more or less accidental discovery of relatively large deposits in faults in the timber. Smith did, however, comment that "the seasoned timber often has white particles filling the cells of the wood, and these are sometimes so plentifully distributed that the planed surface has the appearance of having been filled, to a certain extent, with a substance like plaster of Paris". Mr. M. B. Welch, whose advice we gratefully acknowledge, informed us that this feature is so common in "Colonial Beech" timber that occurrence of the white particles is often used as an aid in identification of the timber. Hence, we selected several pieces of seasoned colonial beech, in which the white particles seemed to occur quite plentifully, and had these planed to very thin shavings. Exhaustive extraction with hot water, as described in the experimental portion, enabled us to recover over 300 grams of pure crystalline gmelinol from 72 superficial feet (120 kilos) of this timber.

After very careful purification the general physical properties described by Smith for gmelinol were confirmed. It melts at 124° (slightly higher than found by Smith), is moderately soluble in hot water but only very sparingly soluble in cold water; almost insoluble in ether and benzene but quite soluble in hot alcohol. Quite large crystals of gmelinol can be grown, and we are able to present a report on these from Miss M. E. Phillips of the Department of Geology of the University of Sydney, which is as follows: " The crystals belong to the orthorhombic system, the faces developed being prisms, macropinacoids and brachydomes. The 100, $\bar{1}00$ faces are well developed, but the 010 face does not appear, being replaced by prisms. The terminations of each crystal consist of the two brachydomes, having indices of the form okl. The value of ρ for these faces is about 45°. Cruciform twinning is well developed in some cases; also a more irregular type which is probably due to intergrowth during crystallisation. The crystals show double refraction and straight extinction for all orientations."

Analyses of gmelinol confirmed the figures given by Smith, who obtained $C=64 \cdot 7$, $64 \cdot 8\%$; $H=6 \cdot 3$, $6 \cdot 6\%$. Our results showed $C=64 \cdot 8$, $64 \cdot 7$, $65 \cdot 2\%$; $H=6 \cdot 0$, $6 \cdot 1$, $6 \cdot 2\%$. Smith assigned to gmelinol the formula $C_{12}H_{14}O_4$ for which theory demands $C=64 \cdot 8$, $H=6 \cdot 3\%$. Apparently he did not consider also the formula $C_{21}H_{24}O_7$ for which theory demands $C=65 \cdot 0\%$, $H=6 \cdot 2\%$. The analyses of derivatives of gmelinol described later all tend to confirm the formula $C_{21}H_{24}O_7$; molecular weight determinations also confirm the latter formula. Smith (*loc. cit.*, p. 196) recorded that " by the freezing point method with acetic acid as solvent, one determination gave 228 as the molecular weight, but with other trials abnormal figures were obtained; this was also the case when boiling chloroform was used as solvent ". Determinations of the molecular weight of gmelinol cryoscopically, using benzene as solvent, gave the following values: 409, 390, 422, 426, 376, 372, 401, 398, 403—mean, 400. Hence, unless gmelinol is associated in benzene it cannot have the formula $C_{12}H_{14}O_4$ assigned by Smith. The molecular weight determinations accord far better with the formula $C_{21}H_{24}O_7$ for which theory demands a molecular weight of 388. In support of this should also be recorded the boiling point of gmelinol, which can be distilled under reduced pressure (only slight decomposition occurring), at 330°/20 mm.

Gmelinol contains methoxyl groups. Smith gave no actual figures for his methoxyl determinations, but stated that " the greatest amount of silver iodide obtained in six determinations only represented about one and three-quarter groups of OCH_3 ". On his formula $C_{12}H_{24}O_4$

this corresponds to a value found for OCH_3 of less than 24%. In our determinations the percentage of methoxyl found was 30·2. Accepting the formula $C_{21}H_{24}O_7$, the presence of four methoxyl groups per molecule would demand a percentage of methoxyl equal to 31·9.

Smith (*loc. cit.*, p. 197) claimed to have proved the presence of one hydroxyl group in gmelinol by acetylation followed by saponification, but we have been unable to repeat his process. Some evidence for the presence of a hydroxyl group was found, however, in the formation of a crystalline phenyl urethane melting at 189°, from which gmelinol can be recovered by hydrolysis. The difficulty of formation of the phenylurethane, and the failure (described below) to obtain any ketonic substance in a chromic acid oxidation experiment, strongly suggest that the hydroxyl group in gmelinol is a tertiary hydroxyl.

Gmelinol can be distilled practically unchanged under reduced pressure, but it breaks down when heated under atmospheric pressure. It was possible to identify veratric acid (formed in small amount only), veratric aldehyde, and, notably, homoveratrole when a portion of gmelinol was destructively distilled. The presence of at least one veratrole nucleus in gmelinol had already been demonstrated by Smith as a result of oxidation experiments.

Perhaps the most outstanding property of gmelinol is its extraordinary sensitivity to acids. Smith noted that it rapidly forms a dark brown amorphous substance when heated with hydrochloric acid. Refluxing with 20% aqueous formic acid solution is sufficient to effect change, and working under these conditions it is possible to isolate in about 50% yield an isomeric substance, isogmelinol, which crystallises in nacreous plates melting at 147°. Isogmelinol is optically active, so that the change brought about by acid treatment is not merely racemization, and isogmelinol is not dl-gmelinol. As is shown later, isogmelinol seems to be more stable than gmelinol.

Oxidation of gmelinol with either aqueous potassium permanganate or chromic acid in glacial acetic acid was found by Smith (*loc. cit.*, pp. 198-199) to lead to formation of veratric acid, and we have been able to confirm this observation. In view of the much larger molecule assigned to gmelinol, and the presence of four methoxyl groups therein, it became of importance to determine whether all the veratric acid obtained on oxidation is derived from the same veratrole nucleus, or whether two such nuclei are simultaneously present in the gmelinol molecule. We were therefore led to attempt quantitative oxidation experiments of gmelinol and of isogmelinol with potassium permanganate, and also of gmelinol with concentrated nitric acid along the lines devised by Robinson and Smith (*Journ. Proc. Roy. Soc. N.S.W.*, 1914, *48*, 460). The yield of pure recrystallised veratric acid in permanganate oxidation of gmelinol was almost exactly equal to the theoretical amount demanded by the presence of one veratryl residue—which strongly suggests the presence of two such nuclei, one hundred per cent. yields in such oxidation processes being extremely difficult to obtain. Oxidation of isogmelinol with permanganate gives a slightly lower yield of veratric acid. Oxidation of gmelinol with nitric acid according to Robinson and Smith's method gave yields of 4 : 5-dinitroveratrole somewhat below the theoretical for one veratryl residue. Oxidation of dibromoisogmelinol (see below) with nitric acid gives only about 60% of the theoretical amount of 4-bromo-5-nitroveratrole required for one veratryl residue. Robinson and Smith, in their nitric acid oxidation of eudesmin obtained a yield of recrystallised 4 : 5-dinitro-veratrole equivalent to 69% of that theoretically required for two veratryl residues, but the effect of constitution on the yield of isolated product is sufficiently indicated by the different yields (percentage) of nitro compounds from gmelinol and dibromogmelinol.

It will also be recalled that Haworth and Kelly (*J.C.S.*, 1937, 385) were unable to isolate yields of oxidation products from lariciresinol dimethyl ether sufficient to establish unequivocally the presence of two veratryl residues in that substance.

Further support for the view that gmelinol does contain two veratryl residues is to be found in the fact that no other isolable product of oxidation except veratric acid has so far been isolated in the permanganate oxidation, whilst the formula $C_{21}H_{24}O_7$ would demand at least one other aromatic nucleus if only one veratryl residue were present, and some product of oxidation of such a nucleus should be able to be readily isolated.

Oxidation of gmelinol in glacial acetic acid with a deficiency of chromic acid, in an endeavour to isolate, if possible, any intermediate ketonic substance, led to production in noticeable quantity of veratric aldehyde, which together with unchanged gmelinol was the only product isolated pure.

Gmelinol can be nitrated in glacial acetic acid solution and a crystalline dinitrogmelinol, $C_{21}H_{22}O_7(NO_2)_2$, melting at 190°, is readily obtained. In contrast to gmelinol itself dinitrogmelinol was insensitive to the action of mineral acids, either aqueous or alcoholic. It was also resistant to oxidation by reagents such as permanganates. Chromic acid reacts vigorously with it in hot glacial acetic acid solution, but, if this oxidation is controlled, it is possible to isolate a substance containing a carbonyl group, which is almost certainly 6-nitroveratric aldehyde. Oxidation of dinitrogmelinol with nitric acid leads to formation of 4 : 5-dinitroveratrole in yield approximately equal to the theoretical for one veratryl residue.

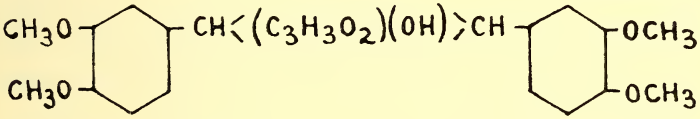
Isogmelinol can also be nitrated in glacial acetic acid, and gives a dinitroisogmelinol melting at 235°.

Bromine in glacial acetic acid has very little action on gmelinol in the cold, but on warming to about 50° hydrogen bromide is eliminated and substitution products are formed. A crystalline dibromo*iso*gmelinol, melting at 196°, is thus formed, together with dibromogmelinol, which is much more difficult to purify. However, if care is taken to prevent the formation of free hydrogen bromide during the bromination, as by bromination of gmelinol in benzene solution in presence of pyridine, no dibromo*iso*gmelinol is formed, but only dibromogmelinol which melts at 145° when pure. Dibromogmelinol and dibromoisogmelinol are unaffected by boiling aqueous alkali, boiling alcoholic alkali, or boiling pyridine. The bromine atoms thus seem definitely to be substituents in aromatic nuclei. Both substances resist oxidation by permanganate. They can be oxidised with concentrated nitric acid, but the only product which can be isolated is 4-bromo-5-nitroveratrole, formation of which seems to argue very definitely for two veratryl residues in gmelinol and isogmelinol, each of which is substituted during bromination.

An observation of great interest is that dibromogmelinol is altered by heating with alcoholic hydrochloric acid to dibromoisogmelinol. This change, which is almost certainly of the same type shown in the gmelinol–isogmelinol isomerisation, cannot be of the ring cyclisation type exhibited by olivil in its conversion to iso-olivil (Vanzetti, *Gazzetta*, 1929, *59*, 373) or by lariciresinol or its ethers in their conversion to isolariciresinol or its ethers (Haworth and Kelly, *loc. cit.*) both of which changes are catalysed by very dilute acids. This is further confirmed by the fact that oxidation of isogmelinol yields veratric acid only, m-hemipinic acid being completely absent from the products of its oxidation.

The reaction of bromine with gmelinol indicates that it is a saturated substance, and this conclusion is confirmed by the fact that gmelinol does not absorb hydrogen in presence of a palladium-norite catalyst. When it is reduced with sodium and boiling absolute ethyl alcohol or with sodium and amyl alcohol it forms a pale yellow, extremely viscous oil which could be distilled unchanged but could not be crystallised. This reduction product is not phenolic, though very small amounts of phenolic material are produced in the sodium amyl alcohol reduction, probably owing to demethylation. The failure to obtain a phenol in this reduction is of considerable interest, as it indicates that gmelinol is not built up on a coumarone or catechin type of molecule with an oxygen heterocyclic ring fused to a benzene ring. Kostanecki and Lampe (*Berichte*, 1907, ***40***, 720) have shown that reduction of catechin with sodium and alcohol gives a phenolic compound in good yield, the coumaran ring being broken in the process.

The available evidence thus far can be summed up as follows: Gmelinol has the molecular formula $C_{21}H_{24}O_7$. This demands a total of 10 rings or double bonds in the molecule. As it resists catalytic hydrogenation and forms substitution products rather than addition products with bromine, any double bonds present must be in aromatic nuclei. Apparently two aromatic veratrole nuclei are present, all the evidence, especially the resistance of dibromogmelinol towards alkalies and its oxidation to 4-bromo-5-nitroveratrole, together with the results of oxidation experiments on gmelinol, indicating the presence of two veratryl residues. These would account for two rings and six double bonds and the four methoxyl groups in gmelinol, leaving a $C_5H_6O_3<$ residue containing two rings to be accounted for. Neither gmelinol, nor the isomeric isogmelinol produced by the action of weak acid on gmelinol gives any reaction for carbonyl, carboxyl, ester, or lactone groups, but gmelinol forms a phenylurethane, albeit with some difficulty, indicating the presence of one alcoholic hydroxyl group. Gentle oxidation with chromic acid in glacial acetic acid gives no ketone corresponding to this alcoholic group, which is probably tertiary. The formation of veratric aldehyde during chromic acid oxidation, and the formation of veratric aldehyde and homoveratrole on destructive distillation argue strongly in favour of the veratryl rests being joined to the $C_5H_6O_3<$ residue through $-CH<$ groups, so that the formula for gmelinol may be expanded to



It is possible to suggest complete structural formulæ in extension of the above expression which formulate the hydroxyl group as tertiary, contain an asymmetrical carbon atom, and give a possible explanation of the great sensitivity of gmelinol to acids ; but we prefer at this stage to postpone consideration of these until we are able to offer more evidence in favour of a complete structural formula.

EXPERIMENTAL.

Isolation of Gmelinol.

Well seasoned planks of *Gmelina Leichhardtii* (" Colonial Beech ", 72 superficial feet) selected for their apparent content of white deposit were reduced to shavings and then extracted with water in a steam-jacketed pan.

To commence the operation two lots of shavings (5 kilos each) were successively extracted with one lot of water (12 gallons), the mixture being maintained at the boiling point for about fifteen minutes. The shavings were removed from the mixture by means of a wire sieve, and filtered in a large Buchner set capable of containing five kilos.

The whole of the liquor was filtered at the second extraction, and then set aside to cool. When perfectly cold the gmelinol was found to have crystallised out on the sides of the pan in the form of a pale brownish yellow crust.

The mother liquor was removed and the gmelinol scraped off. The mother liquor was then used to reextract the shavings already used, which were then rejected, followed by another two fresh lots of five kilos each. This process was repeated, with occasional addition of fresh water to keep up the amount, until 120 kilos of material had been extracted.

As the extraction proceeded it was found to be increasingly difficult to obtain a crystalline deposit owing to the accumulation of impurities. These, however, seemed to be of an acid or phenolic nature, and the addition of as little as 0·05% of sodium hydroxide solution produced a solution giving a beautifully crystalline precipitate. The yield of pure recrystallised gmelinol (recrystallised from an equal weight of alcohol) was 280 grams. The mother liquor on evaporation also yielded quite a large amount (about 200 grams) of tar, which seemed to consist largely of gmelinol.

The recrystallised product formed beautiful colourless prisms, resembling sucrose in appearance, which softened at 122° and melted at 124°. Smith gives the melting point as 122°.

Gmelinol Phenylurethane.

Gmelinol (2 g.) was refluxed with phenyl isocyanate (4 c.c.) for fifteen minutes, and the product poured into ligroin (20 c.c.). After cooling the product was filtered off and recrystallised from a large volume of alcohol or from a mixture of benzene and alcohol. It was obtained as long silky needles, m.p. 189°.

Found: $C=66\cdot7$, $H=6\cdot0$, $N=2\cdot8$, $2\cdot9\%$; calculated for $C_{21}H_{23}O_6.CO.NH.C_6H_5$, $C=68\cdot4$, $H=5\cdot9$, $N=2\cdot8\%$.

Refluxing with excess 10% alcoholic potash solution for one hour led to saponification of this phenylurethane, and gmelinol melting at 124° could be isolated after dilution with water.

Destructive Distillation.

An attempt was made to distil gmelinol destructively at 20 mm., but at this pressure very little decomposition takes place, the substance distilling at about 330°. The distillate was a yellow viscous resin, which on recrystallisation from alcohol was found to be almost entirely gmelinol, together with a little yellow viscous oily material.

Distillation at atmospheric pressure results in breakdown of the molecule. Gmelinol (10 g.) was heated by means of a free flame in a distilling flask. The product consisted of a pale brown oil (5 g.) boiling over a range 200–290°, together with inflammable gas. Distillation of oily material at 23 mm. gave fractions boiling at 120–135° (1·2 g.), 150–170° (1·0 g.) and 170–200° (0·8 g.).

Fraction I possessed a faint odour of eugenol, and was shown to contain a trace of veratric aldehyde by the preparation of the characteristic dinitrophenylhydrazone, m.p. 255° (recrystallised from pyridine). That it consisted mainly of homoveratrole, however, was shown by the preparation in very good yield of the nitro-derivative, nitrohomoveratrole, melting at 118°, by the action of nitric acid in glacial acetic acid.

Micro $N=7 \cdot 05\%$, calculated $N=7 \cdot 1\%$.

This fraction gave no colour with alcoholic ferric chloride.

Fraction II deposited crystalline material, which on recrystallisation from aqueous alcohol melted at 177°. This dissolved in caustic soda solution and showed no depression of melting point on admixture with veratric acid, m.p. 178°.

The remainder of the fraction was dissolved in ether, extracted with dilute caustic soda to remove a small amount of veratric acid, and the ether evaporated. The residue possessed a strong odour of eugenol, but attempts to identify either methyl eugenol or methyl isoeugenol by means of the tribromide or nitrosite were not successful. Oxidation by means of potassium permanganate yielded veratric acid. The fraction was shown to contain veratric aldehyde by the preparation of the characteristic 2 : 4-dinitrophenylhydrazone, m.p. 255°. The fraction gave a pale brown colour with ferric chloride solution.

Fraction III consisted of a viscous pale brown liquid, from which no crystalline material could be obtained. It gave a dark brown coloration with ferric chloride, but contained only a trace of alkali-soluble material.

Isogmelinol.

As stated by Smith, gmelinol soon forms a dark brown resin when heated with mineral acids. However, when it is refluxed with 20% aqueous formic acid for ten hours it is converted into a substance (yield 50%) crystallising from alcohol in pearly plates, melting at 147°, together with tar and other substances not yet investigated. Analysis of the crystalline material showed $C=64 \cdot 0$, $H=6 \cdot 0\%$, so that is it isomeric with gmelinol, and is termed *isogmelinol.*

Isogmelinol is optically active (a solution of 0·5776 g. in 5·9564 g. of chloroform had a rotation of +2°·47 in a 5 c.m. tube). It is thus not merely the racemic form of gmelinol.

Oxidation of Gmelinol.

Smith (*loc. cit.*) showed that oxidation of gmelinol with chromic acid or permanganate led to formation of veratric acid. Attempts were made to determine the number of veratryl nuclei in the gmelinol molecule by means of quantitative oxidation experiments. Oxidations were carried out by means of concentrated nitric acid, the yield of dinitroveratrole being determined; and by means of potassium permanganate, the yield of veratric acid being determined.

Gmelinol (5 g.) was added to nitric acid (D 1·42 ; 15 c.c.), the mixture becoming warm at once, and red fumes being evolved. The oxidation was completed by heating on the water-bath for ten minutes, and then the reaction product was poured into water. The mixture was extracted several times with ether, which on evaporation left a yellow resinous residue. It was found to be very difficult to obtain this material crystalline, but this was finally achieved by first extracting it with boiling 5% caustic soda solution, which removed phenolic impurities, and then crystallising from aqueous alcohol. The yield of crude resin was 2·55 grams and of recrystallised substance was 2·1 grams. The theoretical for one veratryl nucleus is 2·9 grams.

The permanganate oxidation was carried out by stirring gmelinol (4·8 g.) vigorously with water (250 cc.) and gradually adding finely powdered potassium permanganate (12·5 g.) until this ceased to be decolourised. The solution was then acidified by means of dilute sulphuric acid, and sodium bisulphite added to remove the precipitate of manganese dioxide, after which the solution was extracted three times with ether (100 c.c. each time). Evaporation of the dried combined extracts left a pale yellow solid (2·85 g.), which on recrystallisation from alcohol gave veratric acid (2·2 g.). The theoretical amount of veratric acid for one veratryl residue is 2·25 grams.

Oxidation of Gmelinol with Chromic Acid.

Gmelinol (25 g.) was dissolved in glacial acetic acid (150 c.c.) by gentle heat, allowed to cool to about 35°, and chromium trioxide (5 g.), which had been first dissolved in water (10 c.c.), and then acetic acid (25 c.c.) were added. An immediate brown precipitate was produced, which disappeared on standing with evolution of heat, giving a green solution. Most of the acetic acid was distilled off under reduced pressure, and the residue steam-distilled in order to remove veratric aldehyde. Two litres of distillate were collected, which on addition of 2 : 4-dinitrophenylhydrazine sulphate in sufficient sulphuric acid to produce a 2N solution gave a precipitate of veratric aldehyde dinitrophenylhydrazone (4·5 g., m.p. 255°, after recrystallisation from pyridine). The water insoluble resin (A) left after the steam distillation was separated, and the aqueous layer continuously extracted with ether. Only a small amount of material was thus obtained, from which no crystalline product could be obtained, but which contained a trace of veratric aldehyde.

The resin (A) was dissolved in alcohol (200 c.c.) and an insoluble brown precipitate (1·5 g.) filtered off. The precipitate contained organic material, as it would burn, but it left an ash containing chromium. Most of the alcohol was evaporated from the alcoholic solution of the resin (A) and the residue poured into ether. A brown curdy mass was precipitated. After filtration, the alcoholic ethereal solution was evaporated, a pale yellow oil being obtained, which slowly deposited crystals of gmelinol. This oily material was also shown to contain veratric aldehyde by the preparation of the dinitrophenylhydrazone. The brown precipitate obtained above was shown to consist largely of gmelinol (6 g.) by crystallisation from a small amount of alcohol.

Oxidation of Isogmelinol.

Oxidation of isogmelinol (2 g.) by permanganate in a manner similar to that described for the oxidation of gmelinol led to formation of veratric acid (0·8 g.).

Dinitrogmelinol.

This substance was obtained by the action of fuming nitric acid (5 c.c.) dissolved in glacial acetic acid (10 c.c.) on a solution of gmelinol (5 g.) in acetic acid (10 c.c.), at room temperature. After standing for an hour the mixture was diluted with several volumes of water, and the yellow precipitate collected and recrystallised from a large volume of alcohol, in which it is only very sparingly soluble. It was thus obtained as glistening pale yellow leaflets (3·6 g.), which melt at 190°.

Found: C=50·0, 49·5, 50·1, 51·3%; H=4·9, 5·0, 4·8%; N=5·8, 5·8, 5·9, 5·8%. Calculated for $C_{21}H_{22}O_7(NO_2)_2$, C=52·9, H=4·6, N=5·8%.

This dinitro compound is difficult to burn, and this may account for the low carbon values.

A methoxyl determination showed $OCH_3=25\cdot6\%$; calculated for $C_{21}H_{22}O_7(NO_2)_2$, $OCH_3=26\cdot0\%$.

This dinitro compound is optically active. It was recovered unchanged after boiling for a short time with phenyl isocyanate, but prolonged heating produced resinous products. It did not react with 2 : 4-dinitrophenylhydrazine. On reduction with zinc and acetic acid, basic substances, soluble in ether with a violet colour, were obtained. No crystalline product could be isolated. Reduction with hydriodic acid (D 1·7) at 135° resulted in the evolution of methyl iodide and the production of a tar. In contrast to gmelinol itself, the substance was quite unaffected by refluxing for thirty minutes with concentrated hydrochloric acid; and the result cannot be explained by the greater insolubility of the nitro compound, as it is not affected by alcoholic hydrochloric acid, in which it is appreciably soluble. Oxidation of the compound (5 g.) by means of nitric acid (D 1·42) at 100° results in the formation of 4 : 5-dinitroveratrole (2·5 g., m.p. 130°) (phenanthraphenazine by reduction and coupling with phenanthraquinone m.p. 245°). Attempts were made to oxidise the substance with permanganate, but it was found to be unaffected even at 100°. Calcium permanganate in acetone solution was almost without effect, even after boiling for five hours. Chromic acid in glacial acetic acid was also without effect in the cold, but on boiling a vigorous reaction took place.

By less vigorous chromic acid oxidation it was possible to isolate from dinitrogmelinol as main product of the reaction a substance giving a 2 : 4-dinitrophenylhydrazone melting at 260° which very closely resembles the corresponding derivative of 6-nitroveratric aldehyde in colour, solubility, and melting point. The oxidation was carried out as follows:

A solution of chromic oxide (0·27 g.; 1 atom 0) in water (2 c.c.) and glacial acetic acid (10 c.c.) was added to a solution of dinitrogmelinol (2 g.) in glacial acetic acid (25 c.c.). The solution was then warmed on the water-bath for a few minutes. When oxidation appeared to be complete, the acetic acid was removed *in vacuo* and the residue poured into water and the whole extracted with ether. A pale yellow resin was recovered from the ethereal extracts. It gave an immediate red precipitate with dinitrophenylhydrazine sulphate in alcohol. This was collected and recrystallised from pyridine, being thus obtained in minute dark red needles, m.p. 260° (decomp.).

Found: N=17·6%; calculated for $C_{15}H_{13}O_8N_5$, N=17·8%.

Dinitroisogmelinol.

This substance was obtained by a method exactly similar to that used to obtain dinitrogmelinol. After recrystallisation from ethyl acetate it was obtained in very pale yellow needles melting at 235°.

Found: C=53·2, H=5·4, N=6·0%; calculated for $C_{21}H_{22}O_7(NO_2)_2$, C=52·9, H=4·6, N=5·8%.

Bromination of Gmelinol.

A. Gmelinol (10 g.) was dissolved in glacial acetic acid (50 c.c.) by warming and then a solution of bromine (10 g.) in acetic acid (20 c.c.) was added. Evolution of hydrogen bromide commenced, and the reaction was completed by warming on the water-bath for several minutes. Water was then added to precipitate the product, which was obtained as a pale pink amorphous mass. This was recrystallised from ethyl acetate, colourless needles (2 g.), m.p. 196°, being obtained (dibromoisogmelinol). The mother liquor on evaporation gave another substance, which was recrystallised several times from alcohol, and obtained in long silky needles melting rather indefinitely at 135° (5 g.) (dibromogmelinol). Both these substances gave the Beilstein test for halogens. Oxidation of both substances at 100° with nitric acid (S.G. 1·42) gave a substance crystallising in long needles (from alcohol), m.p. 124°, which was identified as 4-bromo-5-nitroveratrole by means of a mixed melting point with an authentic sample. Analysis of dibromoisogmelinol gave C=47·0, H=4·2%; calculated for $C_{21}H_{22}O_7Br_2$, C=46·1, H=4·03%.

B. Gmelinol (5 g.) was dissolved in benzene (25 c.c.) by heating, pyridine (5 c.c.) added, and the mixture cooled to about 40°. Bromine (5 g.) was then slowly added, and the mixture left to stand overnight. The benzene solution was washed several times with water, the benzene evaporated, and the residue recrystallised from a mixture of alcohol and benzene, as white soft needles, m.p. 145°. This closely resembles the material (m.p. 135°) obtained by method (A), but is more easily recrystallised, and melts more sharply.

Found : C$=47 \cdot 0$, H$=4 \cdot 2\%$; calculated for $C_{21}H_{22}O_7Br_2$, C$=46 \cdot 1$, H$=4 \cdot 0\%$.

It does not react with nitric acid in acetic acid in the cold, nor give any crystalline products on further bromination. Heating with nitric acid (S.G. 1·42) yields 4-bromo-5-nitroveratrole (m.p. 124°, mixed m.p. with an authentic sample, 124°).

Bromination of Isogmelinol.

Isogmelinol (2 g.) was dissolved in glacial acetic acid (10 c.c.) and a solution of bromine (2 g.) in acetic acid (5 cc.) run in. The mixture was allowed to stand overnight, and then diluted with water. The pale brown crystalline material was well washed with alcohol and recrystallised from glacial acetic acid. Colourless prisms (2·4 g.), m.p. 196°, mixed m.p. with the substance obtained from the bromination of gmelinol in acetic acid (method A), 196°.

Conversion of Dibromogmelinol to Dibromoisogmelinol.

Dibromogmelinol (1 g.) was refluxed for five hours with a mixture of alcohol (10 c.c.) and concentrated hydrochloric acid (10 c.c.), and the mixture then allowed to stand for a week. It was then diluted with water to about 50 c.c. and the crystals filtered off. The material was recrystallised twice from alcohol, and then melted at 194°, the melting point remaining unchanged by admixture with dibromoisogmelinol (m.p. 196°).

Fusion of Gmelinol with Sodium Hydroxide.

Gmelinol (10 g.) was added to sodium hydroxide (50 g.) containing a few c.c. of water, and the mixture heated in a copper vessel to 220–230° for one hour, stirring by means of an iron-encased thermometer. The gmelinol first melted, forming an upper layer, which gradually became more viscous and darker in colour, gas being evolved.

After an hour the oily layer had become very stiff and pasty, and as it showed no sign of dissolving in the alkali the heating was stopped. The product was completely soluble in water, and on acidification and extraction with ether, phenolic substances were obtained, giving with alcoholic ferric chloride solution a greenish brown colour. No crystalline material could be obtained by fractional precipitation from alcohol by means of water, or by treatment with benzene or ligroin.

Benzoylation by means of the Schotten-Baumann reaction gave no crystalline material.

The formation of phenolic substances is probably due to demethylation.

ACKNOWLEDGMENTS.

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BINUCLEAR ISOMERISM OF DIPHENYL TYPE.

PART III.*

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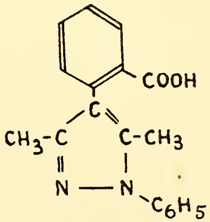
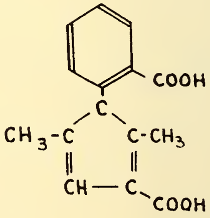
(*Manuscript received, November 17, 1937. Read, December 1, 1937.*)

In this paper there are described briefly the results of certain experiments having as their object the preparation of substances which might be expected to occur in enantiomorphous forms, the enantiomorphism being dependent on restriction of rotation of a cyclic nucleus attached to a benzene nucleus or on restriction of rotation of a group of atoms similarly attached. Two of the authors are unable to continue with the work, and it seems desirable at this point to record the results already obtained and to mention briefly the objects of the investigation which will be continued as soon as opportunity affords.

In the first series of experiments it was proposed to prepare and attempt to resolve 1-phenyl-3 : 5-dimethyl-4-(o-carboxyphenyl) pyrazole (I), which is structurally closely analogous to the 1-(o-carboxyphenyl-2 : 5-dimethyl pyrrole-3-carboxylic acid (II) resolved by Bock and Adams (*J.A.C.S.*, 1931, *53*, 374).



I.



II.

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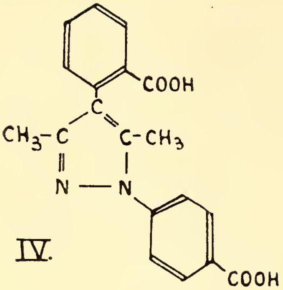
* Part I appeared in THIS JOURNAL, 1930, *64*, 320, Part II in 1933, *67*, 178.

Maclean and Adams (*J.A.C.S.*, 1933, *55*, 4683) have remarked that " from experience gained in the diphenyl series the methyl grouping may be assumed to be relatively large ", and Yuan and Adams (*Chem. Rev.*, 1933, *12*, 261) have also made reference to this point. It would thus appear that (I) should exist in enantiomorphous forms. Now Hurtley (*J.C.S.*, 1929, 1870) has shown that sodium o-bromobenzoate can be readily condensed with sodio acetylacetone in alcoholic solution in presence of copper powder to form the sodium salt of 3-(o-carboxyphenyl)-2 : 4-pentane dione (III) in good yield. We have found that (III) condenses readily with hydrazines to form pyrazoles. Thus, with hydrazine itself 3 : 5-dimethyl-4-(o-carboxyphenyl) pyrazole is rapidly formed. Semicarbazide reacts with (III) to form 3 : 5-dimethyl-4-(o-carboxyphenyl)-pyrazole-1-carboxylic acid amide, a crystalline solid melting at 189° ; whilst with phenylhydrazine the acid (I), melting at 247°, is rapidly formed. Attempts to resolve this acid proved abortive because of its weakness as an acid and inability to form satisfactory alkaloidal salts (cf. Bock and Adams, *J.A.C.S.*, 1931, *53*, 3520).

In consequence, p-carboxyphenylhydrazine was prepared and condensed with (III), so as to obtain 1-(p-carboxyphenyl)-3 : 5-dimethyl-4-(o-carboxyphenyl) pyrazole (IV), a dicarboxylic acid melting at 133° which might reasonably be expected to be strong enough to form stable alkaloidal salts. Preliminary experiments have shown that this is so, and a strychnine salt melting at 187° has been isolated in small amount, but so far not further examined. Several other pyrazoles derived from p-carboxyphenylhydrazine and p-carbethoxyphenylhydrazine are also described in the experimental section.

The second part of the work described in this paper consisted of preliminary exploratory experiments with the object of combining some of the ideas of Chang and Adams with those of Mills and his co-workers. Chang and Adams (*J.A.C.S.*, 1934, *56*, 2089) prepared several meta and para dipyrryl benzenes and effected the resolution of trans-4 : 6-di-(2 : 5-dimethyl-3-carboxypyrryl)-1 : 3-dimethyl benzene (V).

The enantiomorphism of (V) is dependent on the restriction of rotation of the pyrrole nuclei about the bonds joining them to the benzene ring, caused by the methyl groups attached to the benzene ring. It is worthy of



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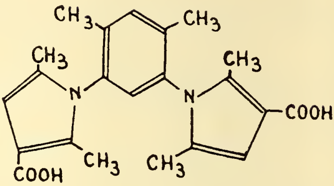
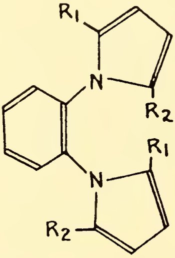


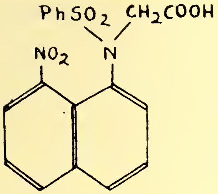
V.

comment that the stability of the enantiomers is very considerable. Chang and Adams did not discuss the possibility of obtaining ortho dipyrrylbenzenes, although the most interesting feature of the structure of such substances would be that the free rotation of each pyrrole nucleus about the bond joining it to the benzene nucleus would be prevented by the second pyrrole nucleus. Thus, a dipyrryl benzene of the formula (VI) should be obtainable in cis and trans modifications of which the latter should exist in enantiomorphous forms. The possibility of preparation of such substances from o-phenylenediamine has not so far been examined.

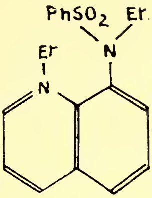


VI.

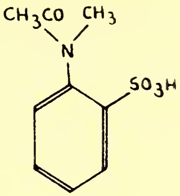
Mills and Elliott (*J.C.S.*, 1928, 1291), Mills and Breckenridge (*ibid.*, 1932, 2209), and, more recently, Mills and Kelham (*ibid.*, 1937, 274) have shown that molecular disymmetry due to restriction of rotation about a single bond can be observed among suitably substituted arylamines such as benzene sulphonyl-8-nitro-1-naphthylglycine (VII), 8-benzene sulphonylethylamino-1-ethyl-quinolinium salts (VIII), and N-acetyl-N-methyl-p-toluidine-3-sulphonic acid (IX). The important necessary condition for restriction of rotation of a disubstituted amino group



VII.

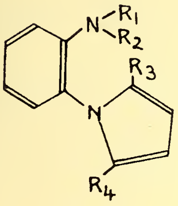


VIII

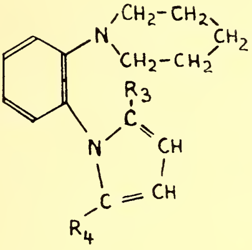


IX.

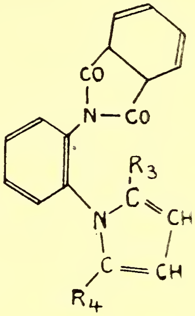
attached to a benzene nucleus is that the " blocking group " in the ortho position should be sufficiently large. Hence it could hardly be doubted that a trans dipyrryl benzene of type (VI) should be resolvable. Further, a disubstituted amino-phenyl pyrrole of type (X) such as a piperidinophenyl pyrrole (XI) or a phthalimidophenyl pyrrole (XII) should exist in enantiomorphous forms, as (XI) and (XII) are types of 2-substituted phenyl pyrroles such as the compound



X.



XI.



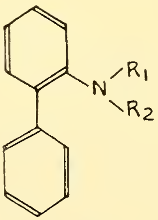
XII.

(II) resolved by Bock and Adams, and the 2-substituent group is relatively large. It is significant that 1-(o-piperidinophenyl)-2 : 5-dimethyl pyrrole (XI ; R_3, $R_4 = CH_3$), which is described in the experimental portion, cannot be induced to form quaternary ammonium salts although it functions as a base. Conversion of the piperidine nitrogen to the 4-covalent state would demand a tetrahedral disposition of the groups around this nitrogen, and owing to the adjacent pyrrole nucleus this demand cannot be satisfied.

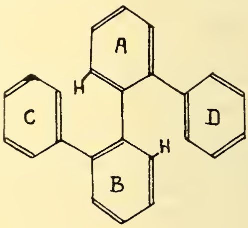
Now in a compound of type (X), whilst free rotation of the pyrrole nucleus will almost certainly be prevented, the possibility that rotation of the disubstituted amino group about the $>$N— benzene link will also be restricted, must be considered, and it should be possible to prepare suitable pyrroles of type (X), where the groups R_3 and R_4 are identical, and the pyrrole nucleus functions simply as a blocking group to prevent the free rotation of the $\genfrac{}{}{0pt}{}{R_1}{R_2}{>}N$— group about the bond joining the nitrogen atom to the benzene nucleus.

It must be remembered that with small groups R_1 and R_2 (Formula X), although the pyrrole nucleus would be a very effective blocking group, *if in the same plane as the benzene ring*, its effectiveness would be markedly diminished when the plane of the pyrrole nucleus is at right angles to the plane of the benzene ring, provided that the pyrrole ring is considered a flat ring of ordinary atomic thickness, i.e. without any " bulge ". Crystal structure measurements show quite clearly that atoms in different molecules of aromatic substances cannot approach each other nearly as much as atoms bound together in the same molecule, and that to all intents and purposes a benzene ring possesses a " bulge " and cannot be considered as a completely flat hexagon. Hence, analogy suggests that the pyrrole ring also would possess some kind of a " bulge ", thus increasing its effectiveness as a blocking group.

It would be important from the point of view of examining the effectiveness of the " bulge " of the benzene ring to prevent free rotation of an ortho nucleus or group to examine some substances of the type (XIII), or even better still to examine certain diphenyl diphenyls of the



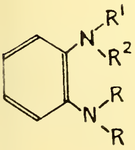
XIII



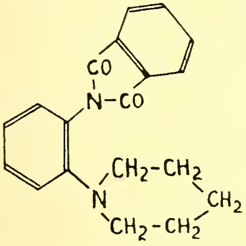
XIV.

type (XIV), in which space demands should prevent all four benzene rings from being simultaneously coplanar. However, rotation of the rings C and D could allow rings A and B to be simultaneously coplanar (i.e. allow free rotation about the bond between rings A and B), provided that the " bulge " on each benzene ring C and D was not sufficiently great to interfere with the ortho hydrogen atoms attached to rings A and B.

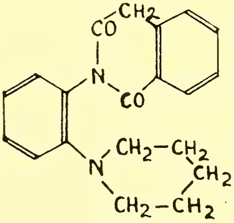
As further examples of the type of substances examined by Mills and Kelham (*loc. cit.*) there should be considered substances of the type (XV). We have prepared o-piperidinophenyl phthalimide (XVI), which is of this type except that R^1 and R^2 are the same (in the phthalimide residue) and also o-piperidinophenyl homophthalimide (XVII). From neither (XVI) nor (XVII) could a quaternary salt be prepared owing to steric hindrance, although both are definite bases. On the other hand 2-acetylaminophenyl piperidine readily forms a methiodide, and it certainly seems probable that (XVII) should be resolvable.



XV.

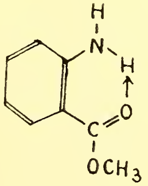


XVI.



XVII.

Finally, we report the synthesis of a few new N-phenyl pyrroles, and further failures to obtain pyrroles from o-nitraniline and methyl anthranilate when treated with 1 : 4-diketones (cf. Hazlewood, Hughes and Lions, *J. Proc. Roy. Soc. N.S.W.*, 1937, *71*, 92). There can be little doubt that the latter of these substances particularly is *chelated* and must almost be regarded as a secondary base, with only one hydrogen atom readily available for substitution. In anthranilic acid, on the other hand, the hydrogen of the carboxyl group is probably concerned in the secondary



valence forces, and the two hydrogens attached to nitrogen are thus available. We also describe the synthesis of 2 : 5-heptanedione, a simple 1 : 4-diketone we propose to use in the synthesis of unsymmetrical N-phenyl pyrroles.

EXPERIMENTAL.

o-Carboxyphenyl acetylacetone (III) was prepared according to the method of Hurtley (*J.C.S.*, 1929, 1870), improvements being effected by using slightly more copper powder, and by removing most of the alcohol from the filtered reaction mixture under reduced pressure before diluting with ice-water and acidifying.

3 : 5-Dimethyl-4-(o-carboxyphenyl)-pyrazole.

Hydrazine hydrate solution (1 c.c. of 50%) was added to a solution of (III) (1 g.) in alcohol (10 c.c.) and the solution boiled under reflux for twenty minutes. The solvent was then removed under reduced pressure, the residue dissolved in a little water and 1 : 1 acetic acid added in very slight excess. The white precipitate formed was collected and recrystallised from dilute alcohol. It came down in colourless prisms melting at 250°.

Found : N = 12·9% ; calculated for $C_{12}H_{12}O_2N_2$, N = 12·6%.

1-Phenyl-3 : 5-dimethyl-4-(o-carboxyphenyl)-pyrazole (1).

Phenylhydrazine (1 g.) was added to a solution of (III) (1 g.) in alcohol (10 c.c.) and the solution boiled under reflux for thirty minutes. Colourless crystals separated on cooling. Recrystallised from alcohol they melted at 247°.

Found : N = 9·8% ; calculated for $C_{18}H_{16}O_2N_2$, N = 9·6%

4-Carboxyphenylhydrazine.

The method of Fisher (*Annalen*, 1882, *212*, 337) was modified in that, after reduction of p-carboxyphenyldiazonium chloride with sulphurous acid and zinc dust and filtration, an equal volume of concentrated hydrochloric acid was added to the filtrate instead of saturating with dry hydrogen chloride. The free hydrazine, also, was recovered from its hydrochloride by addition of sodium acetate solution to its boiling aqueous solution, followed by rapid filtration and allowing to cool, when the base separated in the pure condition.

p-Carbethoxyphenylhydrazine.

Thoms and Ritsert (*Ber. deut. Pharm. Gesellschaft*, 1921, *31*, 65) have prepared this substance but only a brief abstract of their method was available to us. The following method was found to be reasonably satisfactory: A solution of ethyl p-aminobenzoate ("Benzocaine") in dilute hydrochloric acid (55 c.c. of 1·8 N HCl) was carefully diazotised, and the diazo solution run into an ice-cold, saturated solution of sodium sulphite (35 g.). After allowing to stand for fifteen minutes the solution was acidified with acetic acid, excess zinc dust added and the mixture well stirred and gently warmed until the liquid was colourless. It was then filtered and cooled, an equal volume of concentrated hydrochloric acid added and allowed to stand overnight. The precipitated hydrochloride was collected, dissolved in boiling water, sodium acetate crystals (20 g.; excess) added, and after filtration and cooling the filtrate deposited glistening pale yellow plates (3 g.; 30% of theory), which melted at 114° as described by Thoms and Ritsert (*loc. cit.*).

3 : 5-Dimethyl-1-(p-carboxyphenyl)-pyrazole.

Acetylacetone (0·6 g.) and p-carboxyphenylhydrazine (1 g.) were warmed together in alcohol solution (10 c.c.) for thirty minutes. The solvent was then removed under reduced pressure, and the residue treated with water and a slight excess of 1 : 1 acetic acid. The white solid which separated was collected and recrystallised from aqueous alcohol, being obtained in colourless needles, m.p. 158°.

Found: N=13·3%; calculated for $C_{12}H_{12}O_2N_2$, N=13·0%.

1- (p - Carboxyphenyl) - 3 : 5 - dimethyl - 4 - (o-carboxyphenyl)-pyrazole (IV).

p-Carboxyphenylhydrazine (3·2 g.) and (III) (4·5 g.) were dissolved in absolute alcohol (50 c.c.) and heated under reflux for three hours. The alcohol was then removed under reduced pressure, water and a slight excess of dilute acetic acid added, and the mixture cooled in ice. A white crystalline precipitate (6 g.; 90% of theory) separated, was collected and recrystallised from aqueous alcohol and thus obtained as colourless prisms melting at 133°.

Found: $C=67 \cdot 7$, $H=4 \cdot 9$, $N=8 \cdot 5\%$; calculated for $C_{19}H_{16}O_4N_2$, $C=67 \cdot 8$, $H=4 \cdot 8$, $N=8 \cdot 3\%$.

3 : 5-Dimethyl-1-(p-carbethoxyphenyl)-pyrazole.

A solution containing p-carbethoxyphenylhydrazine (1·8 g.) and acetylacetone (1 g.) in alcohol (15 c.c.) was refluxed for thirty minutes, freed of solvent, and the residue treated with water and a little dilute acetic acid. A yellow oil was precipitated but this soon solidified. Recrystallised from aqueous alcohol it was obtained in pale yellow prisms melting at 65°.

Found: $N=11 \cdot 7\%$; calculated for $C_{14}H_{16}O_2N_2$, $N=11 \cdot 5\%$.

1-(p-Carbethoxyphenyl)-3 : 5-dimethyl-4-(o-carboxyphenyl)-pyrazole.

A solution of (III) (1·1 g.) and p-carbethoxyphenylhydrazine (0·9 g.) in alcohol (20 c.c.) was boiled for thirty minutes, then freed from solvent and ice-water added to the residual oil, which then soon solidified. It was recrystallised from aqueous alcohol and obtained in faintly yellow minute prisms melting at 139°.

Found: $N=7 \cdot 8\%$; calculated for $C_{21}H_{20}O_4N_2$, $N=7 \cdot 7\%$.

3 : 5-Dimethyl-4-(o-carboxyphenyl)-pyrazole-1-carboxylic Acid Amide.

To a solution of (III) (1·1 g.) in alcohol (10 c.c.) was added a solution of semicarbazide hydrochloride (0·6 g.) and sodium acetate (0·7 g.) in a little water, and after thorough mixing the mixture was allowed to stand. A precipitate commenced to form after a few hours, and it was collected after 24 hours' standing and recrystallised from boiling water. Minute colourless prisms melting at 189° were obtained.

Found: $N=16 \cdot 4\%$; calculated for $C_{13}H_{13}O_3N_3$, $N=16 \cdot 2\%$.

1 : 3-Diketo-2-(o-piperidinophenyl)-1 : 2 : 3 : 4-tetrahydro isoquinoline (XVII).

Homophthalic acid (18 g.) and 2-aminophenyl piperidine (17·6 g.) were carefully mixed and heated to 180° for fifteen minutes. The mass frothed up and then became a quiescent orange liquid, whilst water was evolved. On cooling, an orange coloured very viscous gum remained which rapidly crystallised on rubbing with cold alcohol. It was recrystallised from boiling alcohol and thus obtained in beautiful colourless prisms which melted at 143°.

Found: $C=74 \cdot 7$, $H=6 \cdot 1$, $N=9 \cdot 0\%$; calculated for $C_{20}H_{20}O_2N_2$, $C=75 \cdot 0$, $H=6 \cdot 3$, $N=8 \cdot 8\%$.

Attempts to prepare quaternary ammonium derivatives of this substance all proved abortive. Addition of one drop of piperidine to a solution of this base (1·5 g.) and benzaldehyde (0·7 g.) in alcohol (20 c.c.) led to darkening in colour and evolution of heat. After standing for two days golden yellow prisms of the *benzylidene derivative* had separated. They were collected and recrystallised from alcohol when they melted at 160-161°.

Found: $C=79 \cdot 2$, $H=5 \cdot 8\%$; calculated for $C_{27}H_{24}O_2N_2$, $C=79 \cdot 4$, $H=5 \cdot 9\%$.

2 : 4-Dinitro-2′-piperidinodiphenylamine.

2 : 4-Dinitrochlorobenzene (10·2 g.) and 2-aminophenylpiperidine (8·8 g.) were mixed and heated together on the water-bath for three hours. The fused mixture rapidly became red in colour. After cooling, the viscous melt was rubbed with alcohol, when it rapidly crystallised in orange crystals. These were treated with ammonia and soon became bright scarlet in colour, owing to formation of the free base, which was collected and recrystallised from alcohol. The base came out in magnificent, gleaming, scarlet needles about one centimetre in length, and is the most beautiful crystalline substance the authors have encountered. It melted at 174°.

Found: $C=59 \cdot 3$, $H=5 \cdot 1$, $N=16 \cdot 6\%$; calculated for $C_{17}H_{18}O_4N_4$, $C=59 \cdot 6$, $H=5 \cdot 3$, $N=16 \cdot 4\%$.

2 : 4-Diamino-2′-piperidinodiphenylamine.

Stannous chloride, hydrochloric acid, and metallic tin in slight excess were added to a solution of the nitro compound in boiling alcohol. After some time the alcohol was boiled off, water added, and the solution treated with decolourising charcoal and filtered. Sodium hydroxide solution in excess was added to the cooled filtrate. The undissolved solid was collected and extracted several times with ether.

The combined ethereal extracts were dried and the ether removed. The residual brownish solid was then crystallised from ethylacetate and obtained in very pale brown prisms melting at 157°.

Found: N=20·3%; calculated for $C_{17}H_{22}N_4$, N=20·0%.

Ethyl-1-veratryl-2-methyl-5-phenyl pyrrole-3-carboxylate.

A solution of ethyl phenacylacetoacetate (2·5 g.) and 4-amino-veratrole (1·55 g.) in alcohol (10 c.c.) and glacial acetic acid (1 c.c.) was refluxed for 90 minutes then poured into water. The brown solid which separated was recrystallised from alcohol with the help of decolourising charcoal and obtained in white glistening plates melting at 115°.

Found: N=3·8%; calculated for $C_{22}H_{23}O_4N$, N=3·8%.

Ethyl-1-(o-carboxyphenyl)-2-methyl-5-phenyl pyrrole-3-carboxylate.

A solution of anthranilic acid (2·75 g.) and ethyl phenacylacetoacetate (5 g.) in alcohol (20 c.c.) and glacial acetic acid (2 c.c.) was heated gently under reflux for nine hours. It was then poured into water and extracted with ether. The solvent was removed from the washed and dried ethereal extract, and the dark brown oily residue which crystallised on standing was recrystallised from acetic acid. It was thus obtained in fine white needles melting at 110°.

Found: N=4·2%; calculated for $C_{21}H_{19}O_4N$, N=4·1%.

Ethyl-1-(o-xenyl)-2-methyl-5-phenyl pyrrole-3-carboxylate.

A solution of 2-aminodiphenyl (1·7 g.), ethyl phenacylacetoacetate (2·5 g.) and glacial acetic acid (1 c.c.) in alcohol (30 c.c.) was refluxed for two hours, then poured into water. A purple oil separated, and was taken up, washed and dried in ether. After removal of the solvent and allowing to stand the residue crystallised and was obtained pure by recrystallisation from boiling alcohol in small colourless prisms melting at 150–151°.

Found: N=3·7%; calculated for $C_{26}H_{23}O_2N$, N=3·6%.

1-(o-Piperidinophenyl)-2 : 5-dimethylpyrrole (*XI* ; R_3, R_4 = CH_3).

An alcoholic solution of equimolecular quantities of acetonylacetone and 2-aminophenylpiperidine containing a little glacial acetic acid was refluxed for two hours, then poured into water. The solid which separated was collected and recrystallised from alcohol and was thus obtained in good yield in small colourless prisms melting at 72°.

Found : N=11·2% ; calculated for $C_{17}H_{22}N_2$, N=11·0%.

This substance fails to give a methiodide with excess methyl iodide in a sealed tube at 100°, and apparently, also, does not form a methosulphate.

1-(o-Piperidinophenyl)-2-phenylpyrrole-5-β-propionic Acid.

A solution of phenacyllævulinic acid (3·5 g.) and 2-aminophenylpiperidine (4·7 g.) in alcohol (25 c.c.) containing glacial acetic acid (2 c.c.) was refluxed for 14 hours, then poured into ice-water. A yellowish brown oil was precipitated, and gradually solidified. It was very soluble in alcohol, acetic acid, acetone, and methyl ethyl ketone but insoluble in water. Eventually it was satisfactorily recrystallised from benzene, m.p. 151°.

Found : N=7·5% ; calculated for $C_{24}H_{26}O_2N_2$, N=7·5%.

The acidic properties of this substance were not very marked. It was not possible to form alkaloidal salts with it.

Ethyl-1-(o-piperidinophenyl)-2-methyl-5-phenylpyrrole-3-carboxylate.

A solution of 2-aminophenylpiperidine (3·5 g.) and ethyl phenacylacetoacetate (5 g.) in alcohol (40 c.c.) containing glacial acetic acid (2 c.c.) was refluxed for three hours, then poured into water. An oily solid separated, and was taken up, washed and dried in ether. After removal of the solvent a very dark oil remained, but this solidified on triturating with alcohol. It was recrystallised from alcohol with the aid of decolourising charcoal and obtained in small white granules melting at 102–103°.

Found : N=7·2% ; calculated for $C_{25}H_{28}O_2N_2$, N=7·2%.

2-Piperidinophenyl-phthalimide (*XVI*).

A method based on those of Rogow (*Berichte*, 1897, *30*, 1442) and Pratt and Perkins (*J.A.C.S.*, 1918, *40*, 207, 216, 225, 1417) was used. A solution of o-aminophenylpiperidine (3·5 g.) and phthalic anhydride (3 g.) in a little acetic acid was refluxed for twenty minutes, then poured into water. The brown solid which separated was collected and recrystallised from alcohol with the help of decolourising charcoal and thus obtained in very pale yellow needles, m.p. 119–120°.

Found : N = 9·1% ; calculated for $C_{19}H_{18}O_2N_2$, N = 9·1%.

Attempts to form the methiodide of this substance by heating it at 100° with excess methyl iodide proved abortive, the base being recovered unchanged. It was also not found possible to prepare a methosulphate.

2-Acetaminophenylpiperidine methiodide.

2-Aminophenylpiperidine was acetylated according to the method of Kuhn (*Berichte*, *33*, 2093) and obtained as a heavy colourless oil boiling at 196–198°/17 mm. Treatment of this substance with methyl iodide in excess in the warm led to rapid formation of a mass of yellow crystals, which were recrystallised from alcohol and thus obtained as small colourless platelets melting at 217–218°.

Found : N = 8·0, I = 34·8% ; calculated for $C_{14}H_{21}ON_2I$, N = 7·8, I = 35·3%.

Ethyl α-acetyl-β-propionyl propionate.

The method employed was an adaptation of Youtz and Perkins's (*J.A.C.S.*, 1929, *51*, 3511–6) modification of the original method of Willstätter and Clark (*Berichte*, 1914, *47*, 291–310) for the preparation of αβ-diacetyl butyric ester. Sodium (48 g.) was finely granulated and stirred with dry ether (200 c.c.). Ethyl acetoacetate (470 g. ; 80% excess) together with dry ether (300 c.c.) was then gradually added (one hour). Stirring was continued until the sodium had dissolved completely (14 hours) more ether (500 c.c.) being added from time to time. 1-Chlorobutan-2-one (237 g.) was then slowly added. The sodium salt appeared to dissolve and after a short time heat was evolved and sodium chloride commenced to precipitate. The stirring of the mixture was continued for a further ten hours. Water was then added, the ether layer separated, washed and dried and the solvent removed. The residual oil was then fractionated *in vacuo*. Most of the excess ethyl acetoacetate was recovered and two fractions boiling at 110–138°/26 mm. (39 g.) and 138–145°/26 mm. (264 g.) were collected. Redistillation of the first fraction afforded a further 20 grams of the second fraction making the total yield approximately 67% of theory. When redistilled ethyl α-acetyl-β-propionyl propionate boils at 140°/26 mm. Its boiling point at 760 mm. is 251°.

Found: C=60·1, H=7·8%; calculated for $C_{10}H_{16}O_4$, C=60·0, H=8·0%.

2 : 5-Heptanedione.

Ethyl α-acetyl-β-propionyl propionate (250 g.) was refluxed for several hours with a solution of potassium carbonate (200 g.) in water (800 c.c.). After cooling, ether was added and the upper layer separated. The aqueous layer was again extracted several times with ether and the combined ethereal extracts were dried and the solvent removed. The residual diketone was then fractionated *in vacuo*. A colourless oil (100 g.; 63% of theory) boiling at 89–92°/21 mm. was collected. On redistillation it boiled constantly at 90°/21 mm. Its boiling point at 760 mm. is approximately 194°.

Found: C=65·3, H=9·2%; calculated for $C_7H_{12}O_2$, C=65·6, H=9·4%.

When treated with semicarbazide this diketone forms a very insoluble semicarbazone melting at 231°.

1-(β-Naphthyl)-2-methyl-5-ethyl pyrrole.

2 : 5-Heptanedione (2 g.) and β-naphthylamine (2·1 g.) were heated for one hour in solution in alcohol (15 c.c.) containing glacial acetic acid (1 c.c.). The solution was then poured into water and the separated solid collected and recrystallised from aqueous alcohol with the help of decolourising charcoal. It formed lustrous colourless plates melting at 102°.

Found: N=6·1%; calculated for $C_{17}H_{17}N$, N=6·0%.

ACKNOWLEDGMENTS.

Some of the (micro) analyses recorded in this paper were carried out by Miss E. M. Goulston, B.Sc., whose help we gratefully acknowledge, as also the assistance of a grant from the Commonwealth Government Research Fund.

We also gratefully acknowledge the assistance of Mr. R. H. Scott in the preparation of 2 : 5-heptanedione.

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HETEROCYCLIC COMPOUNDS DERIVED FROM CATECHOL ETHERS.

PART IV.—SYNTHESIS OF SOME DIMETHOXYBENZACRIDINES.

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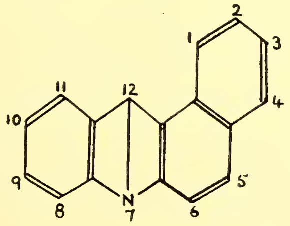
and THOMAS WILKINSON.

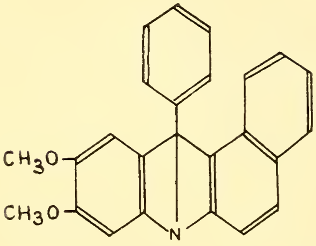
(*Manuscript received, November 17, 1937. Read, December 1, 1937.*)

Among the methods available for the preparation of acridines is the important synthesis of benzacridines from β-naphthol, an aromatic amine and an aldehyde, developed by Ullmann and his co-workers (cf. e.g. Ullmann and Naef, *Berichte*, 1900, *33*, 905–919; Ullmann, Racovitza and Rozenband, *ibid.*, 1902, *35*, 316; D. R. PP. 117472, 119573, 123260). Ullmann, Rozenband, Mühlhauser and Grether (*Berichte*, 1902, *35*, 326) observed that benzaldehyde, β-naphthol, and m-phenylene diamines gave very good yields of benzacridines; and, later, Ullmann and Fitzenkam (*Berichte*, 1905, *38*, 3787) extended the reaction to m-aminophenols and m-aminophenol ethers with almost equal success.

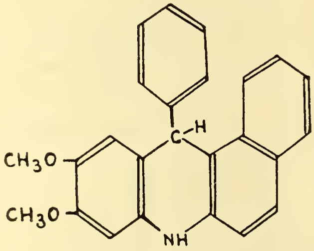
It appeared, therefore, that it should be readily possible to condense 4-aminoveratrole with β-naphthol and various aromatic aldehydes, and so to obtain derivatives of 9 : 10-dimethoxy-1 : 2-benzacridine. (The American Chemical Society's system of numbering has been adopted for the compounds described in this paper.)



Treatment of excess β-naphthol with benzylidene-4-aminoveratrole at 210° for two hours led to formation in good yield of a mixture of 9 : 10-dimethoxy-12-phenyl-1 : 2-benzacridine (I) and 9 : 10-dimethoxy-12-phenyl-7 : 12-dihydro-1 : 2-benzacridine (II). These were readily separated by saturating an ethereal solution of the mixture with dry hydrogen chloride, only the hydrochloride of (I) being precipitated.



I.



II.

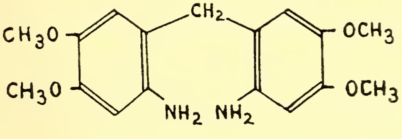
In a similar way, piperonylidene-4-aminoveratrole could be condensed with excess β-naphthol to a mixture of 9 : 10-dimethoxy-12-piperonyl-1 : 2-benzacridine (III) and 9 : 10 - dimethoxy - 12 - piperonyl - 7 : 12 - dihydro - 1 : 2 - benzacridine (IV), but the yields were not so good as with benzaldehyde.

The benzacridines, (I) and (III), thus obtained were pale yellow, high melting crystalline solids, which readily gave salts with picric acid and hydrochloric acid, and also reacted readily with methyl iodide to give the corresponding methiodides.

Attempts to condense benzaldehyde and piperonal with a mixture of 4-aminoveratrole and 4-aminoveratrole hydrochloride to 5-aryl-2 : 3 : 7 : 8-tetramethoxyacridines, according to the method of Ullmann (*Compt. rend. Soc. de Chim. de Geneve*, June, 1898 ; *Berichte*, 1903, *36*, 1017) led to no identifiable products, mainly because of the unstable nature of 4-aminoveratrole. It was also not found possible to condense 4-aminoveratrole with itself in presence of iodine to tetramethoxydiphenylamine, owing to the instability of the base.

Further, condensation of a mixture of 4-aminoveratrole and 4-aminoveratrole hydrochloride with formaldehyde occurs readily, but the only readily isolable product is

2 : 2′-diamino-4 : 5 : 4′ : 5′-tetramethoxydiphenyl methane (V), a base which can be diazotised and coupled with β-naphthol to a red dyestuff, and also readily forms a dihydrochloride and a diacetyl derivative.



V.

Attempts to convert this substance (V) to an acridine derivative were unsuccessful.

EXPERIMENTAL.

Benzylidene-4-aminoveratrole.

Benzaldehyde (29·5 g.) and 4-aminoveratrole (42·5 g.) were heated together out of contact with air on a water-bath for 2½ hours. The resultant dark oil was poured into ice-water and vigorously stirred. It soon solidified and was recrystallised from alcohol being thus obtained in small pale yellow needles, m.p. 71°. Yield, 38 grams.

Found: N=5·9%; calculated for $C_{15}H_{15}O_2N$, N=5·8%.

Piperonylidene-4-aminoveratrole.

Piperonal (16 g.) and 4-aminoveratrole (15 g.) were heated together out of contact with air on a water-bath for 2½ hours. The black oily product was poured into ice-water and vigorously stirred until it solidified. It was then collected and recrystallised from alcohol. Pale yellow needles, m.p. 107°. Yield, 26 grams.

Found: N=4·7%; calculated for $C_{16}H_{15}O_4N$, N=4·9%.

Condensation of Benzylidene-4-aminoveratrole with β-Naphthol.

β-Naphthol (24·9 g.) was melted, and benzylidene-4-aminoveratrole (15 g.) gradually stirred in. When all had been added, the temperature of the melt was raised to 210° and maintained at this for two hours, by which time evolution of water had apparently ceased and the mixture had become quite viscous. After cooling, the melt was dissolved in hot alcohol and the solution poured into aqueous sodium hydroxide solution to remove excess β-naphthol. The precipitated solid (A) was collected and dried, and then extracted with dry ether. The combined ethereal extracts were saturated with dry hydrogen chloride.

9 : 10-Dimethoxy-12-phenyl-1 : 2-benzacridine hydrochloride was precipitated as a yellow powder (9 g.) and was collected. When recrystallised from alcohol it came out in small yellow crystals which melted at 234°. When treated with sodium hydroxide solution it liberated the free base 9 : 10-dimethoxy-12-phenyl-1 : 2-benzacridine (I), a pale yellow substance which was recrystallised from alcohol, and then melted at 205°.

Found: $N=4 \cdot 0\%$; calculated for $C_{25}H_{19}O_2N$, $N=3 \cdot 8\%$.

Admixture of saturated alcoholic solutions of this base (1·9 g.) and picric acid (1 g.) led to production of a golden yellow precipitate of the *picrate*, which was recrystallised from benzene and obtained as a golden yellow powder melting at 289°.

Further, heating of the base (1 g.) with excess methyl iodide in a sealed tube at 100° for twenty minutes led to formation of *9 : 10-dimethoxy-12-phenyl-7-methyl-1 : 2-benzacridinium iodide*, which after recrystallisation from alcohol was obtained in small red-brown prisms melting at 223°.

Found: $I=23 \cdot 1\%$; calculated for $C_{26}H_{22}O_2NI$, $I=23 \cdot 6\%$.

The fraction of the precipitated solid (A) which was insoluble in ether was recrystallised from alcohol. It came down as minute colourless prisms (12 g.) of *9 : 10-dimethoxy-12-phenyl-7 : 12-dihydro-1 : 2-benzacridine*, melting at 198°.

Found: $C=81 \cdot 2$, $H=5 \cdot 6\%$; calculated for $C_{25}H_{21}O_2N$, $C=81 \cdot 2$, $H=5 \cdot 7\%$.

This dihydroacridine was only very slightly soluble in ether, but dissolved readily in other organic solvents. It did not exhibit basic properties, but readily formed an *acetyl derivative* by heating it with an equal weight of acetic anhydride at 100° for half an hour. After pouring into water the precipitated solid was collected and recrystallised from alcohol and obtained as a pale yellow crystalline powder, m.p. 228°.

Found : $C=78\cdot8$, $H=5\cdot4\%$; calculated for $C_{27}H_{23}O_3N$, $C=79\cdot2$, $H=5\cdot6\%$.

Condensation of Piperonylidene-4-aminoveratrole with β-Naphthol.

Piperonylidene-4-aminoveratrole (12 g.) was gradually added to fused β-naphthol (6 g.) and after completion of the addition the temperature was raised to and maintained at 210° for five hours. The melt had by this time become very dark in colour and was quite viscous, reaction apparently being complete. The melt was cooled, powdered, and extracted with dry ether. The ethereal extracts were then separated from the undissolved solid (A′). Saturation of the ethereal extracts with dry hydrogen chloride led to the separation of *9 : 10-dimethoxy-12-piperonyl-1 : 2-benzacridine hydrochloride* as a yellow powder. This could be recrystallised from benzene, alcohol, or dioxane and then melted at 228°.

Found : $Cl=7\cdot7\%$; calculated for $C_{26}H_{20}O_4NCl$, $Cl=7\cdot9\%$.

This hydrochloride was readily soluble in water or alcohol but was only very slightly soluble in ether. Treatment of its alcoholic solution with excess ammonia led to precipitation of the free base *9 : 10 dimethoxy-12-piperonyl-1 : 2-benzacridine* (III) as a yellow powder which was recrystallised from a dioxane water mixture, and was thus obtained in minute yellow prisms melting at 245°. The yield (2 g.) was poor.

Found : $C=76\cdot2$, $H=4\cdot5\%$; calculated for $C_{26}H_{19}O_4N$, $C=76\cdot3$, $H=4\cdot6\%$.

Treatment of an alcoholic solution of this base with alcoholic picric acid led to precipitation of the *picrate*, a very insoluble yellow substance which decomposes at 269°.

The ether insoluble fraction of the crude condensation product (A′) was recrystallised from dioxane. *9 : 10-Dimethoxy-12-piperonyl-7 : 12-dihydro-1 : 2-benzacridine* was thus obtained as a buff powder melting at 242°.

Found : $C=75\cdot4$, $H=4\cdot9\%$; calculated for $C_{26}H_{21}O_4N$, $C=75\cdot9$, $H=5\cdot1\%$.

Treatment of this substance with boiling acetic anhydride for thirty minutes led to formation of *9 : 10-dimethoxy-12-piperonyl-7-acetyl-7 : 12-dihydro-1 : 2-benzacridine* which was obtained as a yellow micro-crystalline powder, m.p, 258° after recrystallisation from alcohol.

Found : N=3·2% ; calculated for $C_{28}H_{22}O_5N$, N=3·1%.

Condensation of 4-Aminoveratrole, 4-Aminoveratrole hydrochloride and Formaldehyde.

Treatment of a mixture of 4-aminoveratrole (10·7 g.) and 4-aminoveratrole hydrochloride (10·7 g.) with 40% formaldehyde solution (3 g.) led to an immediate strongly exothermic reaction, a dark semi-solid mass being produced. This was extracted with dilute hydrochloric acid and the extract basified. A very dark tarry base came out, and was purified by recrystallisation from alcohol with the aid of decolourising charcoal. Small glistening white plates, melting at 140°, of di-(aminoveratryl)-methane (V ; 5·5 g.) were obtained.

Found : C=63·4, H=6·9, N=8·9% ; calculated for $C_{17}H_{22}O_4N_2$, C=64·1, H=6·9, N=8·8%.

Diazotisation of this base, followed by coupling with β-naphthol, led to formation of a red dyestuff. It readily forms a *dihydrochloride* by passing dry hydrogen chloride into its benzene solution. After recrystallisation from alcohol this forms stout white needles melting at 220°.

Found : N=7·3% ; calculated for $C_{17}H_{24}O_4N_2Cl_2$, N=7·2%.

The *picrate* of the base can be obtained by mixing alcoholic solutions of the base and picric acid, and forms a micro-crystalline yellow mass which melts between 190° and 195° with decomposition.

Found : N=13% ; calculated for $C_{17}H_{22}O_4N_2$, $C_6H_3O_7N_3$, N=12·7%.

Treatment of a solution of the base (V) in glacial acetic acid solution with acetic anhydride leads readily to formation of *di-(acetyl aminoveratryl)-methane*, a colourless substance, obtained in needles melting at 219° from alcohol.

Found : N=6·8% ; calculated for $C_{21}H_{26}O_6N_2$, N=6·9%.

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HETEROCYCLIC COMPOUNDS DERIVED FROM CATECHOL ETHERS.

PART V.—SYNTHESIS OF 2 : 3 : 6 : 7-TETRAMETHOXYCARBAZOLE AND SOME DIMETHOXY CARBAZOLES.

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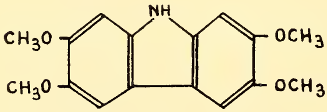
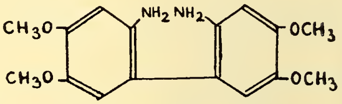
and LESBIA E. ASHCROFT WRIGHT.

(*Manuscript received, November 17, 1937. Read, December 1, 1937.*)

Tauber (D.R.P. 58165; *Berichte*, 1890, *23*, 3266; 1891, *24*, 197, 1033, 2597; 1892, *25*, 128) showed that it is readily possible to prepare carbazole and derivatives of carbazole when 2 : 2′-diaminodiphenyl and its derivatives are heated with 15–20% hydrochloric acid or 25% sulphuric acid at 200°. It thus appeared possible to effect a synthesis of 2 : 3 : 6 : 7-tetramethoxy-carbazole (I) by ring closure with acid of 2 : 2′-diamino-4 : 5 : 4′ : 5′-tetramethoxydiphenyl (II), which is conveniently prepared by reduction with zinc and acetic acid of the corresponding 2 : 2′-dinitro-4 : 5 : 4′ : 5′-tetramethoxydiphenyl (III). This dinitro compound (III), in turn, is readily obtainable by treatment of 4-bromo-5-nitroveratrole with copper powder (*Natur kupfer* C) in the hot, according to the method of Ullmann (cf. *Berichte*, 1901, *34*, 2176).



I.

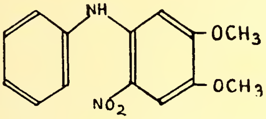


II.

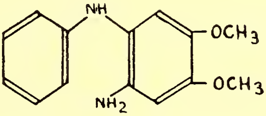
Attempts to convert (II) to (I) by treatment in sealed tubes with hot dilute acids led, apparently, to demethylation and extensive decomposition, only carbonaceous residues being obtained.

Recourse was then had to the second method developed by Tauber (D.R.P. 267833, *Berichte*, 1893, *26*, 1703) for the conversion of 2 : 2′-diaminodiphenyl derivatives to carbazoles, which consists in treatment of the tetrazo compound with 30% potassium sulphide solution. Preliminary attempts to convert (II) to (I) by this method were unsuccessful, but adoption of the conditions suggested by v. Niementowski (*Berichte*, 1901, *34*, 3325) led to a successful preparation of (I), which is a colourless substance melting at 212°.

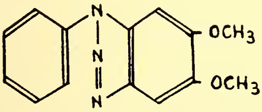
Attention was next directed to the very important Graebe and Ullmann synthesis of carbazoles (*Annalen*, 1896, *291*, 16) which involves the preparation of an ortho-nitrodiphenylamine derivative followed by reduction of this to the corresponding ortho-diamine, which is reacted with nitrous acid to give an aryl aziminobenzene derivative. Distillation of this diazoimide yields the carbazole. We have applied this series of reactions to 2-nitro-4 : 5-dimethoxy-diphenylamine (IV), which is readily prepared from 4-bromo-5-nitroveratrole and aniline. Reduction to the corresponding diamine (V) proved difficult but was eventually achieved satisfactorily. This base (V) has been previously obtained by Jacobsen, Jänicke and Meyer (*Berichte*, 1896, *29*, 2687) as a by-product in the preparation of 3 : 4-dimethoxyazobenzene. The properties of our product agree with those described by Jacobsen, Jänicke and Meyer. Reaction of (V) with nitrous acid in hydrochloric acid solution led to formation of the diazoimide (VI), a dull red crystalline solid melting at 128°. When heated to 300° in a vacuum it lost nitrogen smoothly and



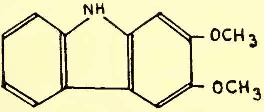
IV.



V.



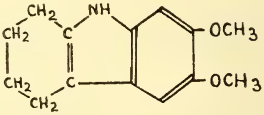
VI.



VII.

2 : 3-dimethoxycarbazole (VII) distilled over and solidified. It formed colourless crystals melting at 125°.

Finally, we have examined a reaction described in D.R.P. 374098 (1923), of which we had only an abstract available, in which it is claimed that quantitative yields of tetrahydrocarbazoles can be obtained by heating together a mixture of an arylamine and 2-chlorocyclohexanone at 150–160°. Attempts to prepare 2 : 3-dimethoxy-5 : 6 : 7 : 8-tetrahydrocarbazole (VIII) by heating 4-aminoveratrole with 2-chlorocyclohexanone either alone or in presence of anhydrous potassium carbonate at 150–160° proved abortive, but condensation occurred readily in presence of anhydrous sodium acetate and (VIII) was obtained as a viscous pale yellow oil boiling at 255°/25 mm. which could be crystallised from petroleum ether and was then obtained as colourless prisms melting at 98° in agreement with Perkin and Rubenstein (*J.C.S.*, 1926, 360).



VIII.

It can be acetylated readily to 9-acetyl-2 : 3-dimethoxy-5 : 6 : 7 : 8-tetrahydrocarbazole, a crystalline solid melting at 136°.

EXPERIMENTAL.

2 : 2′-Dinitro-4 : 5 : 4′ : 5′-Tetramethoxydiphenyl (*III*).

Dry 4-bromo-5-nitroveratrole (20 g.) was heated in a wide-mouthed flask suspended in an oil-bath until a thermometer immersed in the molten nitro compound registered 210°. Copper powder (*Natur kupfer* C, washed free from oil and dried ; 16 g.) was then carefully added in small portions with vigorous stirring. The temperature rose slightly after each addition, but was maintained between 210° and 225°. Addition of the copper powder was complete in about twenty minutes, when the contents of the flask had become very thick. After completion of the addition, the temperature was raised to 240° for a further thirty minutes. After cooling the solidified mass was broken up and repeatedly extracted with boiling benzene. The diphenyl derivative (III) crystallised from the cooled united benzene extracts in glistening yellow prisms (9·8 g.; yield 70%), which melt at 218°.

Found: N=7·7%; calculated for $C_{16}H_{16}O_8N_2$, N=7·7%.

This substance is sensitive to light, the yellow crystals gradually turning red on exposure. It can be readily recrystallised from alcohol, but is best recrystallised from benzene.

2 : 2′-Diamino-4 : 5 : 4′ : 5′-Tetramethoxydiphenyl (*II*).

Zinc dust (10 g.) was gradually added to a vigorously stirred solution of (III) (5 g.) in glacial acetic acid (50 c.c.) and alcohol (20 c.c.), the temperature being maintained at approximately 70°. After completion of the addition the stirring was maintained for a further 90 minutes, the temperature being held at 75°. The pale yellowish brown solution was filtered and cooled and then sodium hydroxide solution (200 c.c. of 20%) was added, and the mixture rapidly extracted twice with chloroform. After washing and drying, the solvents were removed from the combined chloroform extracts, leaving the base (4 g.; yield almost theoretical) as a faintly coloured solid. After recrystallisation from toluene it was obtained in almost colourless needles melting at 180°.

Found: N=9·3%; calculated for $C_{16}H_{20}O_4N_2$, N=9·2%.

Treatment of a cold solution of this base in dilute hydrochloric acid with sodium nitrite followed by alkaline β-naphthol solution leads to formation of a brilliant carmine dye. When its alcoholic solution is treated with alcoholic picric acid a yellow *picrate*, melting at 226° with decomposition, is thrown down.

2 : 3 : 6 : 7-Tetramethoxycarbazole (*I*).

Normal sodium nitrite solution (24 c.c.) was gradually added to an ice-cold solution of (II) (4 g.) in dilute hydrochloric acid (6 c.c. hydrochloric acid to 72 c.c. water). After cooling to −2° this diazo solution was dropped into a well stirred potassium sulphide solution (25 c.c. of 30%) previously cooled to −5°. There was much frothing, and a yellow solid separated. The stirring was continued below 0° for a further fifteen minutes. The reaction mixture was then heated on a boiling water-bath for twenty minutes. After cooling, the separated yellow solid

(3·9 g.; yield almost theoretical) was collected and recrystallised from toluene or from acetic anhydride, being obtained in colourless prisms melting at 212°.

Found: C=66·3, H=5·9%; calculated for $C_{16}H_{17}O_4N$, C=66·9, H=6·0%.

This substance was shown by Lassaigne's test not to contain halogen or sulphur. It did not acetylate easily and could be recrystallised from acetic anhydride unchanged.

2-Nitro-4 : 5-Dimethoxydiphenylamine (*IV*).

4-Bromo-5-nitroveratrole (26·2 g.; 1 mol.), redistilled aniline (22·8 g.; and finely ground anhydrous sodium acetate (8·2 g.; 1 mol.) were mixed and heated for ten hours at 200–210°. The product was then submitted to steam distillation for two hours, and, after addition of concentrated hydrochloric acid, for a further thirty minutes. The water insoluble black residual oil was taken up and recrystallised with the aid of decolourising charcoal from alcohol. After several crystallisations from alcohol orange coloured needles (19 g.; 70% of theory) were obtained, m.p. 91°.

Found: N=10·2%; calculated for $C_{14}H_{14}O_4N_2$, N=10·2%.

2-Amino-4 : 5-Dimethoxydiphenylamine (*V*).

Preliminary attempts to reduce (IV) with zinc dust and acetic acid, or with stannous chloride (cf. Jacobsen, *loc. cit.*) gave only very poor yields of the base (V). Eventually it was obtained in 45% yield by the following process: Tin (24 g.) and concentrated hydrochloric acid (40 c.c.) were added to a solution of (IV) (10 g.) in alcohol (40 c.c.) and the mixture refluxed for two hours. After removal of the excess tin by filtration, much of the alcohol was distilled off and the residual solution cooled in ice. An oily, colourless, heavy substance separated. The clear supernatant liquid was decanted from this oily material, which was taken up in hot alcohol and treated with strong ammonia solution. The heavy white precipitate formed was filtered off and the base (4·3 g.) recovered from the alcoholic filtrate. Recrystallised from aqueous alcohol, it was obtained in colourless prisms melting at 152°. Jacobsen records the melting point as 151°.

1-Phenyl-5 : 6-Dimethoxybenztriazole (*VI*).

A solution of sodium nitrite (0·7 g.) in water (10 c.c.) was gradually stirred into an ice-cold solution of (V) (2 g.) in dilute hydrochloric acid solution (55 c.c. of 0·9 N) containing crushed ice (20 g.). The bluish solution became deep red in colour on addition of the nitrite solution. After completion of the addition the mixture was allowed to stand at 0° for thirty minutes, stirring being continued. A red solid (1·6 g.; 75% of theory) separated and was collected. After recrystallisation from a benzene-petroleum ether mixture it was obtained as a dull red crystalline solid melting at 128°.

Found: N=16·8%; calculated for $C_{14}H_{13}O_2N_3$, N=16·5%.

2 : 3-Dimethoxycarbazole.

The diazoimide (VI; 1·5 g.) was heated in a Claisen flask in a partial vacuum at 300° for ten minutes. The molten liquid frothed considerably, but after ten minutes the frothing ceased and distillation commenced. A slightly yellow oil boiling at 255–260°/25 mm. was collected. It solidified on cooling and was recrystallised from toluene, being thus obtained in practically colourless minute prisms melting at 125°.

Found: N=6·4%; calculated for $C_{14}H_{13}O_2N$, N=6·2%.

2 : 3-Dimethoxy-5 : 6 : 7 : 8-Tetrahydrocarbazole (*VIII*).

2-Chlorocyclohexanone was prepared in 45% yield from cyclohexanol by chlorination in presence of calcium carbonate according to the method of Meyer (*Helv. Chim. Acta*, 1933, *16*, 1291). Preliminary attempts to effect condensation with 4-aminoveratrole in presence of anhydrous potassium carbonate failed completely, although it was possible to condense 2-chlorocyclohexanone with aniline in presence of anhydrous potassium carbonate to tetrahydrocarbazole in good yield. Eventually the following method was proved satisfactory: 2-Chlorocyclohexanone (9 g.) was added to an intimate mixture of finely ground 4-aminoveratrole (10 g.) and anhydrous sodium acetate (7 g.) and the mixture rapidly heated to 170° in an oil bath. A vigorous reaction occurred, accompanied by frothing. After about forty minutes a clear brown quiescent liquid remained. It was cooled and treated with ether and water. The ethereal layer was separated, extracted twice with dilute hydrochloric acid, washed, dried, and the solvent removed. The thick brown oil (9 g.) remaining was distilled *in vacuo*. After a small amount of low boiling material had come over, the tetrahydrocarbazole (VIII) distilled as a very thick and viscous golden yellow oil (6 g.) at 255–260°/25 mm. On cooling it set to a yellow glass, but this was induced to crystallise by rubbing in contact with petroleum ether. Eventually it was recrystallised from petroleum ether and obtained in colourless prisms melting at 98°.

Found: $C=72 \cdot 4$, $H=7 \cdot 3$, $N=6 \cdot 3\%$; calculated for $C_{14}H_{17}O_2N$, $C=72 \cdot 7$, $H=7 \cdot 4$, $N=6 \cdot 2\%$.

9-Acetyl-2 : 3-Dimethoxy-5 : 6 : 7 : 8-Tetrahydrocarbazole.

Refluxing (VIII) with six times its weight of acetic anhydride for six hours, followed by fractionation *in vacuo*, yielded a colourless heavy viscous oil boiling at 220°/2 mm. which set to a clear glass on cooling. On trituration with alcohol it crystallised, and after several recrystallisations was obtained in colourless prisms melting at 136°.

Found: $N=5 \cdot 4\%$; calculated for $C_{16}H_{19}O_3N$, $N=5 \cdot 1\%$.

ACKNOWLEDGMENTS.

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THE NITRATION OF 2-METHOXYDIPHENYL ETHER.

By Francis Lions, B.Sc., Ph.D.,
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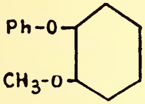
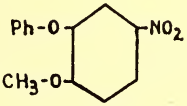
(*Manuscript received, November 17, 1937. Read, December 1, 1937.*)

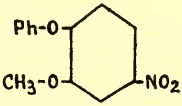
Lea and Robinson (*J.C.S.*, 1926, 412) briefly recorded that 2-methoxydiphenyl ether (I), on nitration in glacial acetic acid solution, gave a solid product which crystallised from alcohol in long colourless needles, m.p. 70–71°, together with an oil which could be precipitated by the addition of water to the alcoholic mother liquor from the recrystallisation. They considered it probable that the solid product was 5-nitro-2-methoxydiphenyl ether (II). This nitration has now again been carefully studied, and the present paper records that the main product of the nitration in glacial acetic acid is 5-nitro-2-methoxydiphenyl ether (II), and that the simultaneous formation of 4-nitro-2-methoxydiphenyl ether (III) in small amount can be demonstrated, these being, most probably, the only two products of nitration.



I.



II.

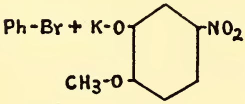


III.

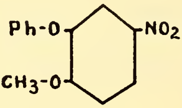
Addition of a solution of nitric acid in glacial acetic acid to a solution of (I) in the same solvent, at a temperature maintained between 25° and 30°, led to smooth nitration. The temperature (15°) recorded by Lea and Robinson (*loc. cit.*) for the nitration of 4-methoxydiphenyl ether was unsuitable, as reaction occurred only very sluggishly at this temperature. By fractional crystallisation and distillation the waxy solid reaction product was separated into a yellow crystalline substance (A) melting at 69° (yield 70%)—presumably identical with Lea and Robinson's crystalline solid melting at 70–71°—and a yellow oil (B) boiling at 190–191·5°/1·7 mm. (yield 30%).

The yellow solid A has been proved to be 5-nitro-2-methoxydiphenyl ether (II). When boiled with aqueous potassium hydroxide solution for three days, it is hydrolysed to a colourless crystalline nitrophenol melting at 63°, a methyl group being lost in the process. Borsche (*Berichte*, 1923, *56*, 1488) has shown that aryloxy groups in the ortho or para positions to a nitro group are much more readily replaced than are alkyloxy groups similarly orientated. It is thus apparent that the nitro group in A is not in the ortho or para position to the phenoxy or o-methoxyphenoxy group, and that it is in either the ortho or para position to the methoxy group. Support for this view is also to be found in the fact that A did not react with piperidine, and consequently cannot possess a nitro group in the ortho or para position to a phenoxy or o-methoxyphenoxy group (cf. Le Fèvre, Saunders and Turner, *J.C.S.*, 1927, 1168).

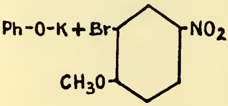
5-Nitro-2-methoxydiphenyl ether (II) was next synthesised by two different methods. In the first, bromobenzene was reacted with the potassium salt of 5-nitroguaiacol (IV) in presence of copper powder to give (II); whilst in the second, 2-bromo-4-nitroanisole (V) was heated with potassium phenate and copper powder to give (II). Comparison of the products (II) obtained by these methods with A showed their identity quite clearly.



IV.

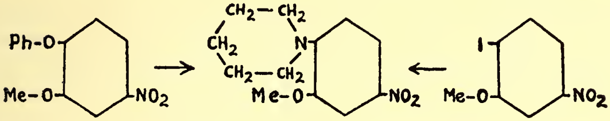


II.



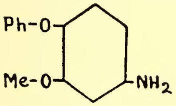
V.

The oil B was found to be a mixture of (II) and (III). When treated with piperidine it immediately reddened, and it was found possible to isolate 1-piperidyl-2-methoxy-4-nitrobenzene (VI), a bright yellow crystalline substance melting at 76°, which had evidently been formed by interaction of (III) with piperidine (cf. Le Fèvre, Saunders and Turner, *loc. cit.*). The identity of (VI) was confirmed by its production from 2-iodo-5-nitroanisole (VII) by interaction with piperidine.

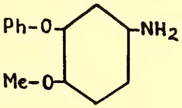


III. VI. VII.

4-Nitro-2-methoxydiphenyl ether (III) was synthesised by heating potassium phenate with 2-iodo-5-nitroanisole (VII) and copper powder and was obtained in rather poor yield as a yellow viscous oil boiling at 175°/0·8 mm. When heated with piperidine it reacted readily to form (VI), identical with the products obtained from the oil B and from (VII) by interaction with piperidine. Further, reduction of the synthetic (III) with boiling aqueous sodium sulphide solution (cf. Fargher, *J.C.S.*, 1920, 869) readily led to production of 4-amino-2-methoxydiphenyl ether (VIII), a very pale yellow crystalline base melting at 119°. Reduction of the oil B by a similar method led to formation of two bases which were separated by fractional crystallisation from petroleum ether. The less soluble was found to be identical with (VIII), whilst the second base was identical with 5-amino-2-methoxydiphenyl ether (IX)—the product of sodium sulphide reduction of (II)—which crystallised in pale pink leaflets melting at 79°. From the relative amounts of the bases (VIII) and (IX) isolated in the reduction of the oil B it would appear that (II) is present in much larger amount than (III) in the oil B, and that consequently only relatively small amounts of (III) (*ca.* 5%) are produced in the nitration under the conditions employed.

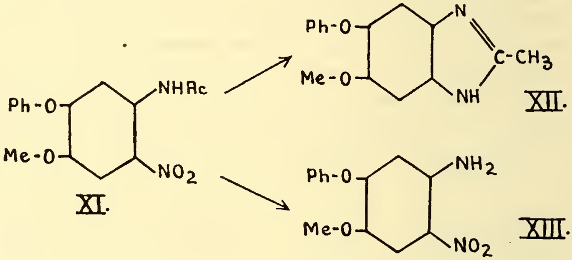


VIII.



IX.

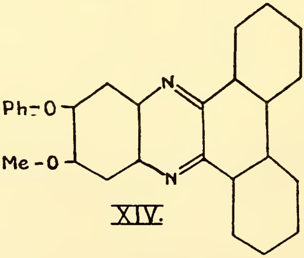
A number of derivatives of (VIII) and (IX) have been prepared, and a support for the constitutions assigned to (II) and (III) and, in turn, to (VIII) and (IX) is forthcoming as a result of these preparations. Thus (IX) is readily formylated, and 5-formylamino-2-methoxydiphenyl ether is a colourless crystalline solid melting at 120°; whilst acetylation of (IX) produces 5-acetylamino-2-methoxydiphenyl ether (X), a colourless crystalline substance melting at 115°, which is readily nitrated in glacial acetic acid solution to 4-nitro-5-acetylamino-2-methoxydiphenyl ether (XI). Reduction of (XI) produces 2-methyl-5-phenoxy-6-methoxybenziminazole (XII) which crystallises from benzene in colourless needles containing benzene of crystallisation, but loses this on heating and then melts at 149°. Hydrolysis of (XI) with hydrochloric acid produces 4-nitro-5-amino-2-methoxydiphenyl ether (XIII), a bright orange-red solid melting at 167°. Reduction of this nitroamine with zinc and aqueous alcoholic hydrochloric acid, followed by treatment of the resulting solution with a solution of phenanthraquinone in aqueous sodium bisulphite solution (cf. Jones and Robinson, *J.C.S.*, 1917, 928) led to formation of 2-methoxy-3-phenoxy-phenanthraphenazine (XIV), which can be obtained in yellow needles melting at 270°.



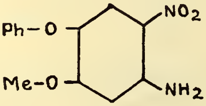
XI.

XII.

XIII.



XIV.



XVII.

In a similar way, VIII was acetylated to 4-acetylamino-2-methoxydiphenyl ether (XV), obtained in needles melting at 138°, which was nitrated in glacial acetic acid to 5-nitro-4-acetylamino-2-methoxydiphenyl ether (XVI), a cream-coloured solid melting at 124°. When this was boiled with aqueous alcoholic hydrochloric acid it hydrolysed to 5-nitro-4-amino-2-methoxydiphenyl ether (XVII), a bright yellow substance melting at 158°. On reduction of this nitro base with zinc dust and hydrochloric acid, and coupling with phenanthraquinone as described for the isomer (XIII), the same 2-methoxy-3-phenoxy-phenanthraphenazine (XIV) was obtained, thus proving the orientation of the nitro groups in the nitroamines (XIII) and (XVI).

Finally, it was observed that nitration of 2-methoxy diphenyl ether with concentrated nitric acid led to formation of a mixture of substances from which it was possible to isolate a trinitro methoxydiphenyl ether melting at 204°. This result is particularly interesting in view of the observations of Scarborough and Sweeten (*J.C.S.*, 1934, 705, 867) that it was not possible to nitrate a mononitrophenyl ether of guaiacol to a trinitromethoxydiphenyl ether, a tetranitro derivative usually being the main product.

EXPERIMENTAL.

Nitration of 2-Methoxydiphenyl Ether in Acetic Acid.

2-Methoxydiphenyl ether (I) was prepared by the method of Ullmann and Stein (*Berichte*, 1906, *39*, 623) and was purified by vacuum distillation, followed by recrystallisation from petroleum ether. It formed colourless needles melting at 78°. To a solution of (I) (40 g.) in glacial acetic acid (200 c.c.) prepared by cooling the hot solution to 25°, was gradually added a solution of nitric acid (D. 1·42 ; 80 c.c.) in glacial acetic acid (100 c.c.) with vigorous stirring, the temperature not being allowed to rise above 40°. After completion of the addition, and allowing to stand a further thirty minutes at room temperature, the mixture was poured on to ice. An oil separated, which set to a yellow waxy solid on standing overnight. This was collected, well washed and dried (49 g.). It was then taken up in ether, washed with water and with sodium carbonate solution and eventually dried and the solvent removed. The residual golden yellow oil partially crystallised on standing and the yellow crystalline solid (24 g.) was separated. Recrystallised from absolute alcohol it came out in pale yellow, prismatic needles (A) melting at 69°. Two further recrystallisations did not raise the melting point.

Found : C=64·6, H=4·7, N=5·7% ; calculated for $C_{13}H_{11}O_4N$, C=63·7, H=4·5, N=5·7%.

The substance A is thus a mononitro-2-methoxydiphenyl ether.

The residual oil (24 g.) was distilled *in vacuo.* Most of it came over in a first fraction boiling at 186–187°/1·5 mm. A second smaller fraction boiling slightly higher—187–187·5°/1·5 mm. was also collected. On standing some crystalline material separated from the first fraction and relatively much more from the second fraction. These crystals were separated (9 g.) and recrystallised from methyl alcohol. They then melted at 69° and their identity with A was shown by mixed melting point determinations. The combined oily residues were again distilled *in vacuo.* An oil (B) came over almost completely (12 g.) between 190° and 191·5°/1·7 mm.

The crystalline product A was found to be identical with 5-nitro-2-methoxydiphenyl ether (II) prepared synthetically (see below). The oily product B was a mixture of 5-nitro-2-methoxydiphenyl ether (II) and some 4-nitro-2-methoxydiphenyl ether (III), as is shown later.

5-Nitro-2-Hydroxydiphenyl Ether.

5-Nitro-2-methoxydiphenyl ether (4 g.) prepared by nitration of (I) (product A) was boiled with a solution of potassium hydroxide (32 g.) in water (200 c.c.) in a copper flask for 72 hours. On cooling, the orange liquid deposited bright yellow needles of the potassium salt of 5-nitro-2-hydroxydiphenyl ether (2·5 g.). These were separated. Acidification of the mother liquor precipitated the nitrophenol (1·3 g.). This was recrystallised from petroleum ether and obtained in very fine, very pale yellow needles melting at 63°. One further recrystallisation from the same solvent produced colourless, very fine needles melting at 63°.

Found: $N=6\cdot1\%$; calculated for $C_{12}H_9O_4N$, $N=6\cdot1\%$.

This nitrophenol dissolves readily in sodium carbonate solution to a bright yellow solution.

5-Nitro-2-Acetyloxydiphenyl Ether.

Addition of acetic anhydride (10 c.c.) to the above described potassium salt (1 g.) followed by gentle warming led to change of colour from yellow to bluish green, and separation of potassium acetate. After heating for 30 minutes, the mixture was poured into water and the white solid obtained after hydrolysis of the excess acetic anhydride was recrystallised from absolute alcohol. It came out in colourless, rod-shaped prisms, or sometimes in glistening white plates, melting at 108°.

Found: N=5·0%; calculated for $C_{14}H_{11}O_5N$, N=5·1%.

Synthesis of 5-Nitro-2-methoxydiphenyl Ether (*II*).

The methods employed were similar to those described by Ullmann and Sponagel (*Berichte*, 1905, *38*, 2211) and Ullmann and Stein (*ibid.*, 1906, *39*, 623).

(*a*) The potassium salt of 5-nitroguaiacol [5 g.; prepared by addition of the calculated amount of potassium hydroxide to 5-nitroguaiacol (Pollecoff and Robinson, *J.C.S.*, 1918, 645) in alcohol] was gently refluxed with bromobenzene (10 c.c.) and copper powder ("*Natur kupfer* C"; 0·25 g.) for 26 hours. Excess bromobenzene was then distilled off in steam, and the residue taken up, washed with alkali, and dried in ether. After removal of the solvent a mass of brown needles (1 g.; 17% of theory) remained. These were rigidly recrystallised from petroleum ether and then melted at 66° alone and at 68° when admixed with the solid A.

Found: N=5·7%; calculated for $C_{13}H_{11}O_4N$, N=5·7%.

(*b*) 2-Bromo-4-nitroanisole (Burns, McCombie and Scarborough, *J.C.S.*, 1928, 2928; 10 g.) and copper powder (0·5 g.) were added to a solution of potassium hydroxide (2·45 g.) in phenol (30 g.) and the whole heated under reflux at 180–200° for 30 hours. The cooled reaction product was treated with ether and excess alkali, and the ether layer separated, washed several times with alkali, dried, and the solvent removed. Crystalline material (2 g.; 20% of the theory) soon separated from the residual oil and after recrystallisation from petroleum ether melted at 69° alone, or admixed with A.

Found: N=5·7%; calculated for $C_{13}H_{11}O_4N$, N=5·7%.

This nitro compound is very soluble in warm methyl and ethyl alcohols, but only sparingly so in the cold; it is very soluble in glacial acetic acid but is only sparingly soluble in petroleum ether. It is not affected by refluxing with excess piperidine.

Synthesis of 4-Nitro-2-Methoxydiphenyl Ether (*III*).

2-Iodo-5-nitroanisole (VII) was prepared from 2-amino-5-nitroanisole (Johnson and Adams, *J.A.C.S.*, 1923, *45*,

1307) by the method of Hanford and Adams (*ibid.*, 1935, *57*, 1592).

Copper powder (0·5 g.) and (VII) (10 g.) were added to a solution of potassium hydroxide (2 g.) in phenol (30 c.c.), and the mixture was heated at 180–200° for 20 hours. After cooling, making alkaline and extracting with ether, the ethereal extract was well washed with sodium hydroxide solution, sodium bisulphite solution, and water, dried, and the solvent removed. The residual oil, distilled *in vacuo*, came over at 175°/0·8 mm. as a yellow viscous oil (1 g.; 12% of the theory) which could not be induced to crystallise.

Attempts to prepare (III) from the potassium salt of 4-nitroguaiacol (Pollecoff and Robinson, *loc. cit.*) and bromobenzene, or iodobenzene in presence of copper powder proved abortive.

1-Piperidyl-2-methoxy-4-nitrobenzene (*VI*).

(*a*) A mixture of piperidine (5 c.c.) and (VII) (2 g.) was very gently refluxed for one hour. The liquid became deep red almost immediately and reaction appeared to be complete in a very short time. Water was added, and brown needles (1·5 g.) separated. These were taken up in dilute hydrochloric acid and treated with sodium bisulphite and charcoal; the solution was filtered off and basified, and the yellow precipitate collected and recrystallised from aqueous alcohol. It came out in yellow needles melting at 76°.

Found: N=12·0%; calculated for $C_{12}H_{16}O_3N_2$, N=11·9%.

(*b*) The oil B (1 g.) was refluxed with piperidine (10 c.c.) for 4½ hours. After cooling and addition of water the oily precipitate was taken up in dilute hydrochloric acid, the solution treated with charcoal, filtered, cooled and basified with sodium hydroxide. The bright yellow precipitate (yield poor) was recrystallised from aqueous alcohol and obtained in needles melting at 76° alone or admixed with the product obtained by method (*a*).

Found: N=12·0%; calculated for $C_{12}H_{16}O_3N_2$, N=11·9%.

5-Amino-2-Methoxydiphenyl Ether (*IX*).

A solution of crystallised sodium sulphide (25 g.) in water (125 c.c.) was added to a solution of (II) (10 g.) in alcohol (50 c.c.) and the mixture was gently refluxed for

3 hours. It turned bright orange in colour. The reaction liquid was then diluted with an equal volume of water. The oil which separated crystallised on cooling. It was taken up in hot dilute hydrochloric acid. On cooling the filtered solution the hydrochloride of the base separated in very pale mauve glistening platelets, melting at 234°. The base itself (7·5 g.; 83% of theory) was obtained by addition of ammonia to the warm acid solution of the hydrochloride as a grey solid, which crystallised from petroleum ether in pale pink leaflets melting at 79°.

Found: N=6·7%; calculated for $C_{13}H_{13}O_2N$, N=6·5%.

5-Acetylamino-2-Methoxydiphenyl Ether (*X*).

Acetic anhydride (3 c.c.) was added to a solution of (IX) (3 g.) in glacial acetic acid (10 c.c.) and the solution refluxed for 30 minutes. Water was then added to incipient precipitation, the solution was boiled and allowed to stand overnight. Very pale mauve, prismatic needles (3·5 g.) separated. After recrystallisation from aqueous alcohol they were obtained practically colourless, melting at 115°.

Found: N=5·5%; calculated for $C_{15}H_{15}O_3N$, N=5·5%.

5-Formylamino-2-Methoxydiphenyl Ether.

A solution of (IX) (0·5 g.) in 90% formic acid (2 c.c.) was heated at 100° for one hour. The amine went into solution, and a deep purple oil separated almost immediately. After cooling the oil was separated, washed with water and then recrystallised several times from aqueous alcohol with the aid of decolourising charcoal. Practically colourless needles melting at 120° were isolated.

Found: N=6·0%; calculated for $C_{14}H_{13}O_3N$, N=5·8%.

5-p-Nitrobenzylidene-amino-2-Methoxydiphenyl Ether.

A solution of (IX) (0·42 g.) and p-nitrobenzaldehyde (0·3 g.) in alcohol (20 c.c.) was refluxed for two hours. Addition of water then caused separation of a yellow solid which was eventually recrystallised from petroleum ether and obtained in bright yellow, feathery micro-crystals melting at 87°.

Found: N=8·1%; calculated for $C_{20}H_{16}O_4N_2$, N=8·0%.

5-o-Nitrobenzylidene-amino-2-Methoxydiphenyl Ether.

This substance was obtained in a manner similar to that for the isomer described above. It crystallised from petroleum ether in beautiful old-gold rhombohedra, melting at 112°.

Found: N=8·2%; calculated for $C_{20}H_{16}O_4N_2$, N=8·0%.

4-Nitro-5-Acetylamino-2-Methoxydiphenyl Ether (*XI*).

A solution of nitric acid (D. 1·42; 1·5 c.c.) in glacial acetic acid (5 c.c.) was gradually added to a solution of (X) (4 g.) in glacial acetic acid (20 c.c.), the temperature being maintained below 25°. The solution became red in colour, and was allowed to stand 30 minutes after completion of the addition. Bright yellow needles separated, and the separation was completed by addition of ice water. The product (yield almost theoretical) was twice recrystallised from absolute alcohol and thus obtained in bright yellow, fibrous needles melting at 141°.

Found: N=9·5%; calculated for $C_{15}H_{14}O_5N_2$, N=9·3%.

2-Methyl-5-Phenoxy-6-Methoxy Benziminazole (*XII*).

Stannous chloride (1 g.) and an excess of granulated tin were added to a solution of (XI) (1·5 g.) in glacial acetic acid (50 c.c.) and the mixture heated under reflux for one hour. The pale yellow solution was decanted from the remaining tin, made strongly alkaline with sodium hydroxide solution and extracted with ether. After washing and drying, the ether was removed leaving a colourless gum which was taken up in benzene. On cooling colourless needles separated. After two further recrystallisations from benzene these melted at 149° if heated slowly. However, if suddenly heated to some such temperature as 125°, they melted immediately to a colourless liquid, which then boiled leaving a deposit melting at 149°. It was thus evident that the white needles from benzene contained benzene of crystallisation. For analysis the needles were heated at 100° for some time, thereby being converted to a fine white powder, m.p. 149°.

Found: N=11·0%; calculated for $C_{15}H_{14}O_2N_2$, N=11·0%.

4-Nitro-5-Amino-2-Methoxydiphenyl Ether (*XIII*).

(*a*) (XI) (2 g.) was boiled with concentrated hydrochloric acid (30 c.c.) for one hour. A red oil separated. After cooling and diluting the oil solidified. It was collected and recrystallised from alcohol, and obtained in dark orange-red octahedra melting at 166°.

(*b*) To a solution of (XI) (1 g.) in alcohol (20 c.c.) were added concentrated hydrochloric acid (5 c.c.) and water (5 c.c.). The solution was then refluxed for two hours. It became bright orange in colour. On cooling, the nitro base (XIII) crystallised out. Recrystallised from absolute alcohol it was obtained in bright orange-red octahedra melting at 167°.

Found: N=10·6%; calculated for $C_{13}H_{12}O_4N_2$, N=10·8%.

4-Amino-2-Methoxydiphenyl Ether (*VIII*).

(*a*) A solution of sodium sulphide (4 g.) in water (20 c.c.) was added to a solution of (III) (prepared synthetically, see above; 1 g.) in alcohol (10 c.c.) and the mixture was heated under reflux for three hours. It became bright red in colour. After cooling, an equal bulk of water was added, the precipitated solid was separated and taken up in dilute hydrochloric acid, treated with charcoal, filtered and basified with ammonia. The precipitated base was recrystallised from petroleum ether and obtained in very pale yellow, prismatic needles melting at 119°.

(*b*) The oil B from the nitration of 2-methoxydiphenyl ether (30 g.) was dissolved in alcohol (150 c.c.) and a solution of sodium sulphide (60 g.) in water (300 c.c.) added. The mixture was then refluxed for three hours. It became bright red in colour. An equal bulk of water was added and the oil which separated solidified on standing. It was taken up in dilute acid, treated with charcoal, filtered, and basified with ammonia. A grey solid separated (20 g.). On recrystallisation from petroleum ether a conglomerate of pink needles and leaflets was obtained which melted partially at 71° but did not liquefy completely till 95°. By redissolving in petroleum ether and fractionally crystallising, (VIII) separated in pale pink needles first, as it had a greater velocity of crystallisation. When leaflets commenced to separate the supernatant liquid was decanted at once. Systematic fractionation eventually led to recovery of 3 grams of pale pink needles melting at 119°, alone or admixed with the base from the synthetic (III).

Found: N=6·8%; calculated for $C_{13}H_{13}O_2N$, N=6·5%.

Careful comparison of the leaflets in the above preparation showed that they were identical with the base (IX) described above, melting at 79°; these two bases appeared to be the only products of reduction of the oil B.

4-Acetylamino-2-Methoxydiphenyl Ether (*XV*).

Acetic anhydride (2 c.c.) was added to a solution of (VIII) (2 g.) in glacial acetic acid (10 c.c.) and the solution refluxed 30 minutes. Addition of water then caused separation of an oil which was induced to crystallise. It was eventually obtained after repeated recrystallisation from aqueous alcohol in very pale mauve needles melting at 138°.

Found: N=5·5%; calculated for $C_{15}H_{13}O_3N$, N=5·5%.

5-Nitro-4-Acetylamino-2-Methoxydiphenyl Ether (*XVI*).

A solution of nitric acid (D. 1·42; 0·5 c.c.) in glacial acetic acid (2 c.c.) was added to a solution of (XV) (1 g.) in glacial acetic acid (7 c.c.) at room temperature. The solution reddened. After standing 30 minutes, water was added and the precipitated yellow solid collected and recrystallised from alcohol. It was thus obtained in long, velvety, cream-coloured needles melting at 124°.

Found: N=9·4%; calculated for $C_{15}H_{14}O_5N_2$, N=9·3%.

5-Nitro-4-Amino-2-Methoxydiphenyl Ether (*XVII*).

(XVI) (1 g.) was dissolved in alcohol (20 c.c.) and hydrochloric acid (5 c.c.) and water (5 c.c.) added. The solution was then refluxed for three hours. It became orange in colour. On cooling, the base (XVII) crystallised out in clusters of bright yellow needles, and after recrystallisation from alcohol these melted at 158°.

Found: N=10·6%; calculated for $C_{13}H_{12}O_4N_2$, N=10·8%.

2-Methoxy-3-Phenoxyphenanthraphenazine (*XIV*).

Zinc dust in excess was slowly added to a solution of either (XIII) or (XVII) (0·5 g.) in alcohol (10 c.c.) and concentrated hydrochloric acid (3 c.c.). The solution became deep red in colour, then green and finally pale yellow. Water was added, the solution boiled and filtered hot and then saturated with sodium acetate. A solution of phenanthraquinone (1 g.) in aqueous sodium bisulphite was now added and the mixture boiled for five minutes. The precipitate which formed was collected and recrystallised from either acetone or xylene, very small yellow needles melting at 270° being obtained.

Found : N=6·8%; calculated for $C_{27}H_{18}O_2N_2$, N=7·0%.

The solution of this phenanthraphenazine in concentrated sulphuric acid has an intense cerise colour. Its solutions in acetone or xylene are deep yellow, and have a faint greenish fluorescence. (XIV) thus appears to be an exception to the general rule of Jones and Robinson (*J.C.S.*, 1917, 910) who stated that " the ethers of 1 : 2-dihydroxyphenanthraphenazine are bright yellow and exhibit green fluorescence in benzene or other neutral solvent, whilst the ethers of 2 : 3-dihydroxyphenanthraphenazine are faintly yellow and yield almost colourless solutions with intense violet fluorescence."

Nitration of 2-Methoxydiphenyl Ether with Concentrated Nitric Acid.

Nitric acid (D. 1·42 ; 100 c.c.) was added in one lot to (I) (10 g.), which dissolved with evolution of heat, production of a red brown colour and production of nitrogen peroxide. After standing 48 hours, the reaction mixture was heated at 100° for one hour. After cooling, the nitric acid layer was decanted from the oil which had separated, and this was washed several times with water. On addition of ether, it crystallised immediately in yellow cubes (6 g.). On recrystallisation several times from benzene, a pale yellow substance crystallising in prismatic needles melting at 204° was eventually isolated.

Found : N=12·6%; calculated for $C_{13}H_9O_8N_3$, N=12·5%.

The substance is thus a trinitro-2-methoxydiphenyl ether.

ACKNOWLEDGMENTS.

Some of the (micro) analyses recorded in this paper were carried out by Miss E. M. Goulston, B.Sc., whose help we gratefully acknowledge, as also the assistance of a grant from the Commonwealth Government Research Fund.

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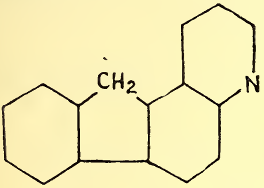
DERIVATIVES OF 5 : 6-INDENO (2 : 1) QUINOLINE.

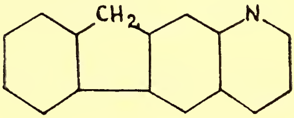
By Gordon K. Hughes, B.Sc.,
Francis Lions, B.Sc., Ph.D.,
and Lesbia E. A. Wright.

(*Manuscript received, November 17, 1937. Read, December 1, 1937.*)

Diels and Staehlin (*Berichte*, 1902, *35*, 3275) applied the Skraup reaction to 2-aminofluorene and showed that an indenoquinoline was formed, but they were unable to decide between formula A and formula B for their substance. Apparently only one quinoline derivative was formed, indicating definite predisposition towards ring closure in a particular way.



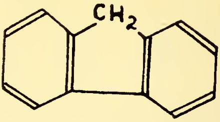
A.



B.

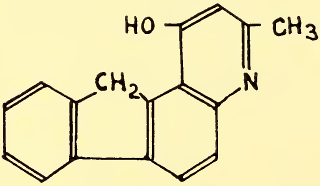
Very recently, Hughes, Le Fèvre and Le Fèvre (*J.C.S.*, 1937, 202) have discussed the structures of fluorene and fluorenone without coming to a definite pronouncement in favour of any one particular formula, but they have pointed out the marked resemblance of fluorene to cyclopentadiene and to indene, and the contrast between fluorene and diphenylmethane. It does not seem unfair, therefore, to formulate fluorene as containing a cyclopentadiene ring (C), and if this is accepted, Diels and Staehlin's indenoquinoline must be formulated as A. Without any other basis than this we have formulated the derivatives of indenoquinoline described in this paper as derivatives of 5 : 6-indeno (2 : 1) quinoline.

2-Aminofluorene (I) condenses readily at 100° with ethyl acetoacetate in presence of a very small amount of hydro-

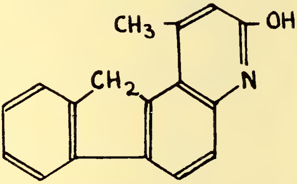


C.

chloric acid (cf. Coffey, Thomson and Wilson, *J.C.S.*, 1936, 856) to form ethyl β-(2-fluorenylamino)-crotonate, a yellow crystalline substance melting at 96°, which cyclises rapidly in hot paraffin oil at 280° to 1-hydroxy-3-methyl-5 : 6-indeno (2 : 1) quinoline (II), a colourless crystalline substance which does not melt below 290°. When dropped into excess ethyl acetoacetate previously heated to 160°, (I) reacts vigorously with elimination of alcohol and formation of 2-acetoacetamidofluorene, a pale yellow solid melting at 146° (cf. Limpach, *Berichte*, 1931, *64*, 970). This cyclises in the usual way when dissolved in five times its weight of cold concentrated sulphuric acid with formation of 1-methyl-3-hydroxy-5 : 6-indeno (2 : 1) quinoline (III). Ethyl cyclohexanone-2-carboxylate also condenses



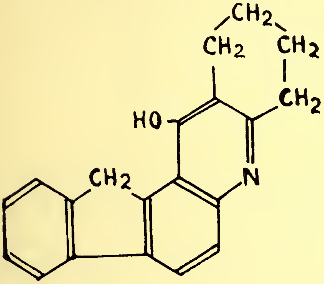
II.



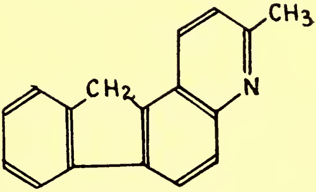
III.

readily with (I) at 100° in presence of a very small amount of hydrochloric acid, and the ethyl 1-(2′-fluorenylamino)-$\triangle^1$ cyclohexene-2-carboxylate so formed cyclises readily in hot paraffin oil to 13-hydroxy-1 : 2 : 3 : 4-tetrahydro-8 : 9-indeno (2 : 1) acridine (IV), a crystalline substance of low solubility which does not melt below 300°.

2-Aminofluorene can be induced to undergo the Döbner-Miller quinoline synthesis, also, without difficulty. When it is heated with paraldehyde, hydrochloric acid and zinc chloride a vigorous reaction occurs at 70°, and from the clear viscous red syrup so formed it is possible to isolate 3-methyl-5 : 6-indeno (2 : 1) quinoline (V) as a colourless crystalline substance which melts at 133–135°. (V) readily forms a crystalline methiodide melting at 243°.

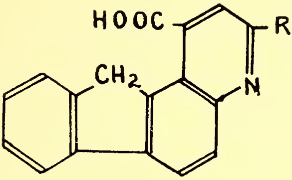


IV.



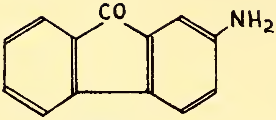
V.

2-Aminofluorene also readily undergoes the Döbner pyruvic acid synthesis of quinolines. Addition of an alcoholic solution of (I) to a boiling alcoholic solution of pyruvic acid and benzaldehyde leads to rapid formation of 3-phenyl-5 : 6-indeno (2 : 1) quinoline-1-carboxylic acid (VI ; $R{=}C_6H_5$), which crystallises out from the reaction liquid very soon. Similar products are readily obtained from (I) and pyruvic acid with piperonal and anisaldehyde.

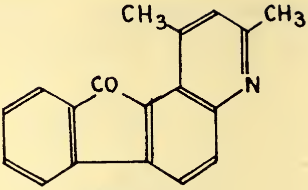


VI.

We have also carried out some syntheses of quinoline derivatives from 2-aminofluorenone (VII). Diels and Staehlin (*loc. cit.*) showed that 2-aminofluorenone readily undergoes the Skraup quinoline synthesis. It is now shown also that it can undergo the Combes synthesis. It condenses readily with acetylacetone to form β-(2-fluorenonylamino)-propenyl methyl ketone, a substance crystallising in orange needles which melt at 146° and which dissolves in excess cold concentrated sulphuric acid forming 1 : 3-dimethyl-11-keto-5 : 6-indeno (2 : 1) quinoline (VIII), a red crystalline substance melting at 126°.



VII.



VIII.

2-Aminofluorenone can also be condensed with aldehydes (such as benzaldehyde and piperonal) and pyruvic acid in alcoholic solution to form the indenocinchoninic acids, 3-phenyl-11-keto-5 : 6-indeno (2 : 1) quinoline-1-carboxylic acid (IX ; $R=C_6H_5$) and 3-piperonyl-11-keto-5 : 6-indeno (2 : 1) quinoline [IX ; $R=C_6H_3(O_2CH_2)$], both well crystallised substances. An attempt to prepare a hydroxyquinaldine from 2-aminofluorenone and ethyl acetoacetate was not successful, mainly because of the unstable nature of the intermediate β-arylaminocrotonic ester.

EXPERIMENTAL.

β-(*2-Fluorenylamino*)-*crotonate.*

2-Aminofluorene was prepared by the method described in " Organic Syntheses ", Vol. XIII, p. 74.

2-Aminofluorene (9 g.) and ethyl acetoacetate (6·5 g.) were heated together to a homogeneous melt at 100° and one small drop of 1 : 1 hydrochloric acid added. Water commenced to separate soon afterwards, but heating was continued for two hours. The mass solidified on cooling and was recrystallised several times from methanol, being obtained in pale yellow crystalline aggregates, m.p. 96°. The yield was almost quantitative.

Found : C=77·3, H=6·1% ; calculated for $C_{19}H_{19}O_2N$, C=77·8, H=6·1%.

1-Hydroxy-3-methyl-5 : 6-indeno (*2 : 1*) *quinoline* (*II*).

β-(2-Fluorenylamino)-crotonate (5 g.) was dropped into paraffin oil (50 g.) previously heated to 280°. A vigorous reaction occurred, alcohol boiled off, and the quinoline separated in the crystalline condition. After cooling the solid was collected, washed thoroughly with ether, and recrystallised from much alcohol, being thus obtained in fine colourless prisms which did not melt below 290°. The alcoholic solutions exhibited a blue fluorescence.

Found : $C=81\cdot5$, $H=5\cdot0\%$; calculated for $C_{17}H_{13}ON$, $C=82\cdot5$, $H=5\cdot2\%$.

The *picrate* of this base was obtained by mixing an alcoholic solution with alcoholic picric acid. It formed bright yellow needles which melted at 231° (decomp.).

Found : $N=11\cdot4\%$; calculated for $C_{23}H_{16}O_8N_4$, $N=11\cdot8\%$.

2-Acetoacetamidofluorene.

2-Aminofluorene (4·0 g.) was slowly added to ethyl acetoacetate (16 g.) at 160°. The base dissolved and a brisk evolution of alcohol vapour occurred, the solution acquiring a deep orange colour. On cooling a yellow gelatinous solid was obtained. It was freed from excess ethyl acetoacetate by pressing between filter papers, and recrystallised from alcohol, again coming out as a gelatinous solid, which was eventually dried and powdered. It then melted at 145–146°.

Found : $C=77\cdot5$, $H=5\cdot7\%$; calculated for $C_{17}H_{15}O_2N$, $C=77\cdot0$, $H=5\cdot3\%$.

1-Methyl-3-hydroxy-5 : 6-indeno (2 : 1) quinoline.

The above described acetoacetarylide was dissolved in five times its weight of ice-cold concentrated sulphuric acid, a dark green solution being obtained. It was allowed to stand some time and was then poured on to ice, a cream-coloured precipitate being thrown out. Dilute ammonia was added in excess when the solid changed colour to pale pink. It was collected, well washed and recrystallised from 80% aqueous alcohol and thus obtained in very fine colourless crystals melting at 265° with decomposition.

Found : $C=83\cdot5$, $H=5\cdot5\%$; calculated for $C_{17}H_{13}ON$, $C=82\cdot5$, $H=5\cdot2\%$.

Ethyl-1-(2′-fluorenylamino)-Δ^1-cyclohexene-2-carboxylate.

2-Aminofluorene (4 g.) and ethyl cyclohexanone-2-carboxylate (3·2 g.) were heated together at 100°, and to the homogeneous mixture one drop of 1 : 1 hydrochloric acid was added ; heating was continued for two hours. The mass solidified on cooling and was recrystallised from methanol, pale yellow prisms melting at 110° being obtained in almost quantitative yield.

Found : $C=78\cdot8$, $H=7\cdot0\%$; calculated for $C_{22}H_{23}O_2N$, $C=79\cdot3$, $H=6\cdot9\%$.

13-Hydroxy-1 : 2 : 3 : 4-tetrahydro-8 : 9-indeno (*2 : 1*) *acridine* (*IV*).

The above described product of condensation from 2-aminofluorene and ethyl cyclohexanone-2-carboxylate was added to ten times its weight of paraffin oil at 290°. A vigorous reaction occurred and the tetrahydroacridine derivative (IV) separated in excellent yield as an insoluble solid. After cooling it was collected, freed from paraffin with ether, and recrystallised from pyridine. It came out in very fine rod-shaped needles which did not melt below 300°.

Found : C=83·0, H=5·7% ; calculated for $C_{20}H_{17}ON$, C=83·6, H=5·9%.

3-Methyl-5 : 6-indeno (*2 : 1*) *quinoline* (*V*).

This substance was prepared by a method similar to that used by Nair and Simonsen (*J.C.S.*, 1926, 3140) for preparation of the quinaldine from aminoacenaphthene. 2-Aminofluorene (21 g.), hydrochloric acid (D 1·19 ; 40 g.), paraldehyde (30 g.) and anhydrous zinc chloride (1·5 g.) were warmed together. The mass, which was grey in colour, became deep red at 70° and a vigorous reaction occurred. After keeping at 100° for a further ninety minutes the clear viscous red syrup was boiled up with two successive lots of dilute hydrochloric acid (2·5 N ; 500 c.c. each time) for an hour. A solution of sodium nitrite (10 g.) in water (30 c.c.) was then slowly stirred into the combined acid extracts, and the tarry material which separated was removed by filtration. The clear hot solution was then slowly added to excess of ice-cold dilute ammonium hydroxide solution. The thick almost tarry oil which separated was taken up, washed and dried in benzene and after removal of the solvent was distilled *in vacuo*, a fraction (10 g.) boiling between 210 and 220° at 2·2 mm. being collected. It solidified on cooling, and after recrystallisation from alcohol was obtained in very fine colourless crystals which appeared to melt indefinitely between 145° and 159°.

Found : C=88·0, H=5·3% ; calculated for $C_{17}H_{13}N$, C=88·3, H=5·6%.

Heat treatment of this quinaldine derivative (V ; 3 g.) with methyl iodide (12 g. ; excess) in a closed tube at 100° for fifteen minutes led to formation of the *methiodide*, a yellow crystalline solid, which melted at 243° (decomp.) after recrystallisation from aqueous alcohol.

Found : I=34·4% ; calculated for $C_{18}H_{16}NI$, I=34·0%.

3-Phenyl-5 : 6-indeno (2 : 1) quinoline-1-carboxylic acid (*VI* ; *R*=C_6H_5).

The method employed was based on that of Döbner (*Berichte*, 1894, *27*, 352, 2020) and Halberkann (*ibid.*, 1921, *54*, 3090). A boiling solution of 2-aminofluorene (9 g.) in alcohol (80 c.c.) was gradually added to a boiling solution of pyruvic acid (4·4 g.) and benzaldehyde (6 g.) in alcohol (40 c.c.). The yellow crystalline cinchoninic acid crystallised out almost immediately. After one hour's heating it was collected (yield, 65% of theory). It was very insoluble but could be recrystallised from nitrobenzene at 150°. When heated, it darkened at 250° and melted at 272°.

Found : C=81·9, H=4·5% ; calculated for $C_{23}H_{15}O_2N$, C=81·9, H=4·5%.

3-Piperonyl-5 : 6-indeno (2 : 1) quinoline-1-carboxylic acid (*VI* ; *R*=$C_6H_3O_2CH_2$).

This substance was obtained in 70% yield from 2-aminofluorene (9 g.), pyruvic acid (4·4 g.) and piperonal (8 g.) exactly as described for the previous preparation. It was recrystallised from pyridine and obtained as a yellow finely crystalline substance which darkened at 220° and appeared to decompose at about 245°. Its solution in pyridine showed a brilliant blue fluorescence.

Found : C=75·7, H=4·4% ; calculated for $C_{24}H_{15}O_4N$, C=75·6, H=4·0%.

3-(p-Anisyl)-5 : 6-indeno (2 : 1) quinoline-1-carboxylic acid (*VI* ; *R*=*p*-C_6H_4-OCH_3).

This substance was obtained by an exactly similar method. It formed fine yellow crystals which dissolved in pyridine with brilliant blue fluorescence. These darkened and appeared to decompose at about 255°.

Found : C=78·2, H=4·7% ; calculated for $C_{24}H_{17}O_3N$, C=78·4, H=4·6%.

2-Aminofluorenone (*VII*).

This base was prepared according to the method of Diels (*Berichte*, 1901, *34*, 1764). It forms a *dinitro-*

phenylhydrazone, very fine red needles, which darkens at 265° and appears to melt at 287°.

Found: N=18·0%; calculated for $C_{19}H_{13}O_4N_5$, N=18·6%.

β-(*2-Fluorenonylamino*)*-propenyl methyl ketone.*

2-Aminofluorenone (4 g.) and acetylacetone (2 g.) were heated together at 100° and a trace of hydrochloric acid added. Water separated, and after heating for one hour the oil was cooled. It solidified to an orange mass, which was recrystallised from alcohol and obtained in gleaming orange needles melting at 145–146° (yield, 85% of theory).

Found: C=77·6, H=5·1%; calculated for $C_{18}H_{15}O_2N$, C=78·0, H=5·4%.

1 : 3-Dimethyl-11-keto-5 : 6-indeno (*2 : 1*) *quinoline* (*VIII*).

The above described Schiff's base (2 g.) was gradually dissolved in ice-cold concentrated sulphuric acid (10 g.) and the deep red solution warmed to 50° for thirty minutes. The acid solution was then poured into ice-cold dilute ammonium hydroxide solution, when a purplish coloured precipitate formed. It consisted partly of 2-aminofluorenone, and the base (VIII), a pale red crystalline solid, which after six recrystallisations from alcohol melted at 126°.

Found: C=83·0, H=4·9%; calculated for $C_{18}H_{13}ON$, C=83·4, H=5·0%.

3-Phenyl-11-keto-5 : 6-indeno (*2 : 1*) *quinoline-1-carboxylic acid* (*IX*; $R=C_6H_5$).

A hot solution of (VII) (3·8 g.) in alcohol (40 c.c.) was gradually added to a boiling solution of pyruvic acid (2 g.) and benzaldehyde (2·5 g.) in alcohol (20 c.c.). During one hour's heating the cinchoninic acid separated as a crystalline orange precipitate (yield 50%), which, after recrystallisation from pyridine, was obtained in fine deep yellow prisms, which darkened at 185° and melted with decomposition at 205°.

Found: C=78·3, H=3·8%; calculated for $C_{23}H_{13}O_3N$, C=78·6, H=3·7%.

3-Piperonyl-11-keto-5 : 6-indeno (*2 : 1*) *quinoline-1-carboxylic acid* [*IX*; $R=C_6H_3(O_2CH_2)$].

This was obtained in a similar manner from (VII), pyruvic acid, and piperonal in alcohol, and after recrystallisation from pyridine formed very fine yellow crystals, which did not melt below 290°.

Found : C=72·4, H=3·2% ; calculated for $C_{24}H_{13}O_5N$, C=72·9, H=3·3%.

ACKNOWLEDGMENTS.

Some of the (micro) analyses recorded in this paper were carried out by Miss E. M. Goulston, B.Sc., whose help we gratefully acknowledge, as also the assistance of a grant from the Commonwealth Government Research Fund.

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DERIVATIVES OF 4-HYDROXYQUINOLINE.

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and Francis Lions, B.Sc., Ph.D.

(*Manuscript received, November 17, 1937. Read, December 1, 1937.*)

Roberts and Turner (*J.C.S.*, 1927, 1832) have discussed some of the factors controlling the formation of derivatives of quinoline, particularly by the Combes process. Their work showed that it was possible to prepare certain 2 : 4-dimethyl quinolines by the Beyer synthesis which could not be obtained by the Combes synthesis. Hence, it becomes obvious that, although substituents in the benzene ring can exercise an influence against quinoline ring formation which may be sufficiently great to prevent ring closure completely in certain reactions, by variation of the type of reaction successful ring closure may be effected. We have been greatly struck with the ease of formation of highly crystalline derivatives of quinoline—the 4-hydroxyquinaldines—which are obtainable from arylamines and ethyl acetoacetate by the method of Conrad and Limpach (*Berichte*, 1887, *20*, 944, 948 ; Limpach *ibid.*, 1931, *64*, 969-70), and have prepared several new substituted compounds of this type which are described in the experimental section. We have also made use of the similar reaction for the preparation of 1 : 2 : 3 : 4-tetrahydroacridones, in which arylamines are condensed in presence of a trace of 1 : 1 hydrochloric acid with ethyl cyclohexanone-2-carboxylate to ethyl 1-arylamino-$\triangle'$-cyclohexene-2-carboxylates, which are then cyclised by dropping into hot paraffin oil. This reaction appears first to have been used by Blount, Perkin and Plant (*J.C.S.*, 1929, 1977) and by Sen and Basu (*Journ. Indian Chem. Soc.*, 1930, *7*, 435). The substances so far prepared are described in the experimental section, and, apart from commenting that we were able to prepare the tetrahydroacridone from p.aminoacetanilide (Sen and Basu reported failure to effect cyclisation of the intermediate from this base), we prefer to reserve a theoretical discussion of our accumulated results for the present, whilst recording the synthesis and properties of the derivatives so far made.

EXPERIMENTAL.

The general procedure was as follows: Equimolecular parts of the amine and the β-keto ester (4 gms.) were mixed and one drop of hydrochloric acid (1 : 1) was added; evidence of reaction taking place was shown by the formation of globules of water, which usually took place within ten minutes. In some cases the reaction was started by gentle warming on the water bath. The mixtures were allowed to stand overnight. If the intermediate unsaturated arylamino ester crystallised it was filtered off and recrystallised from a suitable solvent, usually methyl alcohol. If not crystalline the intermediate ester was taken up and dried in ether, and the solvent removed. The intermediates were cyclised by first warming to 100° and then adding them to liquid paraffin (50 c.c.) previously heated to 280°. The hydroxyquinoline derivative which usually crystallised within a minute or so from the hot solution, was collected after cooling, freed from paraffin with the help of petroleum ether and recrystallised from a suitable solvent, usually much alcohol.

TABLE 1.

Intermediate Aryl-amino-Δ'-cyclo-hexene-2-carboxylic esters from Ethyl cyclo hexanone-2-carboxylate.

Amine.	Crystalline Form of Intermediate.	Solvent of Recrystallisation.	M.P.	Molecular Formula.	Analysis.	
					Found.	Calc.
o.Toluidine ..	Large white prisms.	Methyl alcohol.	84°	$C_{16}H_{21}NO_2$	% C 74·3 H 8·0	% C 74·1 H 8·1
p.Bromaniline	Small white needles.	,,	78°	$C_{15}H_{18}NO_2Br$	N 4·45	N 4·3
p.Xenylamine	Glistening white plates.	,,	107°	$C_{21}H_{23}NO_2$	C 78·8 H 7·2	C 78·5 H 7·2
o.Anisidine ..	White prisms.	,,	80°	$C_{16}H_{21}NO_4$	C 69·7 H 6·4 N 5·1	C 69·8 H 7·6 N 5·1
p.Anisidine ..	Pale yellow prisms.	,,	71°	$C_{16}H_{21}NO_3$	C 69·8 H 7·7 N 5·4	C 69·8 H 7·6 N 5·1
p.Phenetidine	Pale yellow prisms.	,,	87°	$C_{17}H_{23}NO_3$	C 70·8 H 8·0	C 70·6 H 8·0
p.Amino benzoic acid ..	Yellow plates.	,,	166°	$C_{16}H_{19}NO_4$	C 66·3 H 6·6	C 66·5 H 6·6
3-Amino-acenaphthene	Yellow needles.	Ethyl alcohol.	122°	$C_{21}H_{23}NO_2$	C 79·0 H 7·0	C 78·5 H 7·2

Table II.

Substituted Tetrahydro-Acridones from Ethyl cyclo hexanone-2-carboxylate.

Amine.	Crystalline Form.	Solvent of Recrystallisation.	M.P.	Molecular Formula.	Analysis.	
					Found.	Calc.
o-Toluidine ..	Small white needles.	Ethyl alcohol.	>300°	$C_{14}H_{15}NO$	% C 78·7 H 7·2	% C 78·9 H 7·0
p-Toluidine ..	White needles.	,,	>300°	$C_{14}H_{15}NO$	C 78·6 H 6·8	C 78·9 H 7·0
o-Anisidine ..	White platelets.	,,	278°	$C_{14}H_{15}NO_2$	C 73·7 H 6·3	C 73·4 H 6·5
p-Anisidine ..	Small needles.	,,	284°	$C_{14}H_{15}NO_2$	N 6·3	N 6·1
o-Phenetidine	White prisms.	,,	237°	$C_{15}H_{17}NO_2$	N 6·0	N 5·8
p-Phenetidine	White needles.	,,	>300°	$C_{15}H_{17}NO_2$	C 74·1 H 7·0	C 73·8 H 6·9
α Naphthyl-amine.	White prisms.	,,	>300°	$C_{17}H_{15}NO$	C 81·2 H 5·8	C 81·2 H 6·0
β Naphthyl-amine.	Pale yellow plates.	,,	>300°	$C_{17}H_{15}NO$	C 82·3 H 5·8	C 81·2 H 6·0
o-Xenylamine	White powder.	Methyl alcohol.	200°	$C_{19}H_{17}NO$	N 4·2	N 4·2
p-Xenylamine	White needles.	,,	>300°	$C_{19}H_{17}NO$	C 82·9 H 5·4	C 82·8 H 5·3
p-Nitraniline	Pale yellow needles.	Ethyl alcohol.	>300°	$C_{13}H_{12}N_2O_3$	N 11·5	N 11·7
p-Brom-aniline	Pale yellow prisms.	Butyl alcohol.	>300°	$C_{13}H_{12}NOBr$	N 5·1	N 5·0
o-Chlor-aniline	Small white needles.	Ethyl alcohol.	260°	$C_{13}H_{12}NOCl$	N 5·9	N 6·0
p-Chlor-aniline	White needles.	,,	>300°	$C_{13}H_{12}NOCl$	C 66·7 H 5·1	C 67·0 H 5·0
2-4-di-Chlor-aniline.	,,	,,	296°	$C_{13}H_{11}NOCl_2$	N 5·3	N 5·2
p-Amino benzoic acid.	,,	,,	>300°	$C_{14}H_{13}NO_3$	C 69·5 H 5·6	C 69·4 H 5·4
Ethyl p-amino benzoate.	Yellow needles.	,,	>300°	$C_{16}H_{17}NO_3$	C 71·0 H 6·5	C 70·8 H 6·3
3 - Amino - acenaphthene	Pale yellow plates.	,,	>300°	$C_{19}H_{17}NO$	C 82·9 H 5·4	C 83·1 H 5·2
p-Amino acetanilide.	Yellow prisms.	,,	>300°	$C_{15}H_{16}N_2O_2$	C 69·8 H 5·1	C 70·3 H 6·2
p-Xylidine ..	Small white needles.	,,	255°	$C_{15}H_{17}NO$	C 79·3 H 7·5	C 79·2 H 7·3

TABLE III.

4 Hydroxyquinaldines from Ethyl aceto-acetate.

Amine.	Crystalline Form of Quinoline.	Solvent of Recrystallisation.	M.P.	Molecular Formula.	Analysis.	
					Found.	Calc.
p.Bromaniline	Small white needles.	Ethyl alcohol.	>300°	$C_{10}H_8NOBr$	% N 5·9	% N 5·9
m-Brom aniline	Pale yellow platelets.	,,	>300°	$C_{10}H_8NOBr$	C 49·9 H 3·4	C 50·3 H 3·4
o-Xenylamine	White powder.	Methyl alcohol.	280°	$C_{16}H_{13}NO$	C 82·3 H 5·7	C 81·7 H 5·5
p-Amino acetanilide.	Small prisms.	Ethyl alcohol.	>300°	$C_{12}H_{12}N_2O_2$	N 12·9	N 13·0
o-Chlor aniline	Pale yellow needles.	Methyl alcohol.	220°	$C_{10}H_8NOCl$	N 7·0	N 7·2
2 . 4 Dichlor aniline.	White needles.	Ethyl alcohol.	290°	$C_{10}H_7NOCl_2$	N 6·4	N 6·2

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HETEROCYCLIC COMPOUNDS DERIVED FROM 5- AND 8-AMINOQUINOLINES.

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Gordon K. Hughes, B.Sc.,
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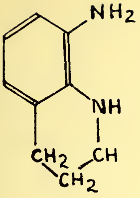
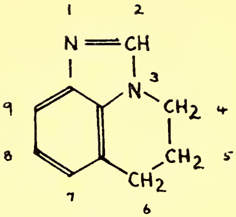
8-Aminoquinoline can be reduced with sodium and alcohol to 8-amino-1 : 2 : 3 : 4-tetrahydroquinoline (I), an oily base which is virtually a N : 6-dialkylated orthophenylene diamine. The marked ease with which o-phenylene diamine itself forms benziminazole and quinoxaline derivatives is well known, and it became of interest to examine whether the further binding of one of the nitrogen atoms of the orthophenylene diamine molecule to the benzene nucleus by a trimethylene chain would affect its power to form heterocyclic derivatives of the benziminazole and quinoxaline types. Jackson and Kenner (*J.C.S.*, 1928, 573), in a very full discussion, have pointed out that there is much evidence to show that substances can be obtained in which a five- and six-membered ring, one at least of which is reduced, can be simultaneously fused to a benzene nucleus in such a way that one atom not in the benzene ring is common to both. In consequence, it was anticipated that (I) would behave as a typical N-monoalkylated ortho phenylene diamine. Evidence is now presented in proof of this contention. When treated with formic acid under reflux (I) readily forms 1 : 7-trimethylene benziminazole (II) for which we suggest the systematic name 5 : 6-dihydroquinolo-1 : 3-diazole, the parent ring compound and its numbering being shown in (III).

In a similar way, from acetic, propionic, and phenylacetic acids there are readily obtained 2-methyl-(IV ; R $=CH_3$), 2-ethyl- (IV ; R $=C_2H_5$) and 2-benzyl-5 : 6-dihydroquinolo-1 : 3-diazoles (IV ; R $=CH_2.C_6H_5$), which may also be named respectively 2-methyl-, 2-ethyl-, and 2-benzyl-1 : 7-trimethylene benziminazoles.



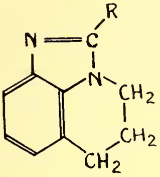
I.

II.

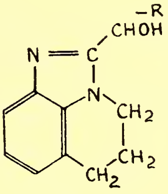


III.

In a similar way, and perhaps even more readily, (I) reacts with glycollic acid to form 2-hydroxymethyl-5 : 6-dihydro-quinolo-1 : 3-diazole (2-hydroxymethyl-1 : 7-trimethylene benziminazole (V; R=H); whilst lactic acid and mandelic acid give the corresponding 2-α-hydroxyethyl-(V; $R=CH_3$) and 2-α-hydroxybenzyl-5 : 6-dihydro-quinolo-1 : 3-diazoles (V; $R=C_6H_5$). With benzilic acid (I) reacts readily forming 2-α-hydroxybenzhydryl-5 : 6-dihydro-quinolo-1 : 3-diazole (2-α-hydroxybenzhydryl-1 : 7-trimethylene benziminazole). All these derivatives of benziminazole are beautifully crystalline solids.



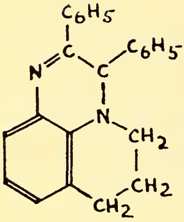
IV.



V.

o-Phenylene diamine reacts readily with α-keto alcohols, such as benzoin, to form 2 : 3-disubstituted quinoxaline dihydrides (cf. O. Fischer, *Berichte*, 1891, *24*, 720; Hinsberg, König, *ibid.*, 1894, *27*, 2181), and this reaction is also readily given by N-monosubstituted o-phenylene diamines. Fusion of (I) with benzoin leads readily to formation of 2 : 3-diphenyl-1 : 8-trimethylene-1 : 2-dihydro-quinoxaline (VI), which we have also named as a derivative of quinolo-1 : 4-diazine (VII), viz., 2 : 3-diphenyl-6 : 7-dihydroquinolo-1 : 4-diazine.

Pyruvic acid condenses readily with (I), also, to form 2-methyl-3-keto-6 : 7-dihydroquinolo-1 : 4-diazine (VIII), a crystalline solid melting at 113°.



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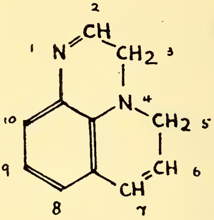

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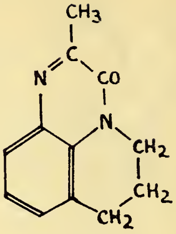
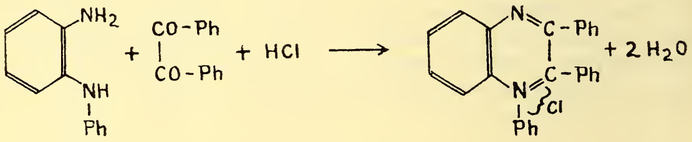
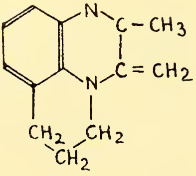


VIII.

O. Witt (*Berichte*, 1892, *25*, 1017 Anm.) examined the reaction of N-monoarylated ortho phenylene diamines on α-diketones, and showed that, for example, N-phenyl o-phenylene diamine hydrochloride reacted with benzil to form a " stilbazonium chloride ", according to the scheme.



We were unable to isolate satisfactory products of this type from the hydrochloride of (I) and benzil. The reaction of (I) with diacetyl also seemed to be abnormal, it not being possible to isolate 3-methyl-2-methylene-1 : 7-trimethylene-1 : 2-dihydroquinoxaline (IX) from the reaction mixture as might be anticipated (cf. Kehrmann and Messinger, *Berichte*, 1892, *25*, 1627, 1866 ; Decker and Hock, *ibid.*, 1904, *37*, 1568). However, it was possible to obtain 8 : 9-trimethylene flavine (X) by condensation of (I) with alloxan in glacial acetic acid containing boric acid (cf. Kuhn and Weygand, *Berichte*, 1935, *68*, 1282).



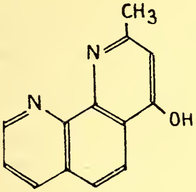
IX.

X.

Treatment of an equimolecular mixture of (I) and ethyl acetoacetate with a trace of 1 : 1 hydrochloric acid led to elimination of water and formation of ethyl β-(8′-tetrahydroquinolylamino) crotonate. When this was dropped into hot paraffin oil it lost an acetic acid residue and was converted to the 2-methyl-5 : 6-dihydroquinolo-1 : 3-diazole (IV ; R=CH_3), which is also obtained by condensation of (I) with acetic acid. That the ring closure should occur in this way rather than that a phenanthroline derivative should be formed is of particular interest.

We have examined the possibility of formation of derivatives of o-phenanthroline from 8-aminoquinoline (because of their great interest in co-ordination work) by utilisation of reactions other than the Skraup reaction. The Combes synthesis fails completely, although the intermediate β-(8′-quinolylamino) propenyl methyl ketone is readily obtained. Cyclisation of 8-acetoacetamidoquinoline with sulphuric acid to a 2-hydroxy lepidine derivative also fails. More success attended the preparation of 2-methyl-4-hydroxy-1:10-phenanthroline (XI) which was obtained by the usual method from 8-aminoquinoline and ethyl acetoacetate as a high melting crystalline solid.

In a similar way we have prepared 7-hydroxy-9-methyl-4 : 10-phenanthroline (XII) ; and also, the hydroxy-



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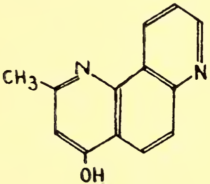
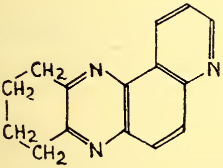
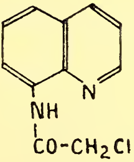


XII.



XIII.



XIV.

XV.

tetrahydroacridine (XIII) from the condensation of 5-aminoquinoline with ethyl acetoacetate and ethyl cyclohexanone-2-carboxylate respectively.

Finally, it is to be recorded that 8-aminoquinoline reacts with chloracetyl chloride in chloroform solution to form the hydrochloride of 8-chloracetylaminoquinoline (XIV). Heat treatment of the base (XIV) leads to formation of the cyclic quaternary ammonium salt, 8 : 1-anhydroglycollylaminoquinolinium chloride (XV).

EXPERIMENTAL.

8-Aminoquinoline.

In the preparation of this substance by reduction of 8-nitroquinoline with iron filings and dilute acetic acid, considerable loss of material is avoided if the crude 8-aminoquinoline is purified by vacuum distillation rather than by recrystallisation from ligroin or water as recommended in the literature. It boils at 174°/26 mm. and at 164°/19 mm.

8-Amino-1 : 2 : 3 : 4-tetrahydroquinoline.

8-Aminoquinoline (25 g.) was dissolved in boiling alcohol (600 c.c. ; distilled from calcium) in an efficient reflux apparatus and metallic sodium (45 g.) added as rapidly as possible. The liquid cleared slightly in colour. When almost all of the metal had dissolved steam was passed to remove the alcohol and the distillation was continued until an oily upper layer about five mm. in depth had separated. The mixture was then rapidly cooled, contact with air being minimised and the oil taken up, washed and dried in ether. After removal of the solvent it was distilled *in vacuo.* A clear faintly yellow liquid boiling at 145°/2 mm. (23 g.) was collected. It darkened very rapidly on exposure to air and was usually immediately sealed in ampoules. Owing to this tendency to oxidise it was analysed as the picrate.

The picrate, formed in alcoholic solution, recrystallised in fine brownish-yellow needles, m.p. 178° from alcohol.

Found : $C=48\cdot6$, $H=4\cdot3$, $N=18\cdot9\%$; calculated for $C_{15}H_{15}O_7N_5$, $C=47\cdot6$, $H=4\cdot2$, $N=18\cdot6\%$.

5 : 6-Dihydro-quinolo-1 : 3-diazole (*II*).

A solution of 8-aminotetrahydroquinoline (2·5 g.) in glacial formic acid (D 1·22 ; 20 g.) was gently refluxed for two hours. After cooling with ice the solution was made alkaline with ammonia and the oil which separated taken up, washed and dried in ether and the solvent removed. The residual oil crystallised on contact with petroleum ether and was recrystallised from this solvent, being thus obtained in colourless rectangular plates and prism clusters, m.p. 148°.

Found: $N = 17 \cdot 8\%$; calculated for $C_{10}H_{10}N_2$, $N = 17 \cdot 7\%$.

2-Methyl-5 : 6-dihydro-quinolo-1 : 3-diazole. (IV; $R = CH_3$.)

8-Aminotetrahydroquinoline (2·5 g.) and acetic anhydride (20 g.) were refluxed together for two hours and then poured on to ice. The mixture was basified with ammonia. The oil which separated soon solidified and was recrystallised from aqueous alcohol. It came out in stout needles containing water of crystallisation, which was readily lost in a vacuum. Crystallised from petroleum ether the anhydrous material came out in needles melting at 128°.

Found: $N = 16 \cdot 3\%$; calculated for $C_{11}H_{12}N_2$, $N = 16 \cdot 2\%$.

2-Ethyl-5 : 6-dihydro-quinolo-1 : 3-diazole. (IV; $R = C_2H_5$.)

A solution of 8-aminotetrahydroquinoline (1 g.) in propionic acid (12 g.) was refluxed for four hours, then poured on to ice and basified with ammonia. The separated oil was taken up, washed and dried in ether, and after removal of the solvent distilled *in vacuo*. A colourless oil boiling at 195°/20 mm. was collected. It solidified almost at once on cooling. It had a pronounced smell reminiscent of both propionic acid and acetamide. After recrystallisation from ether it melted at 86°.

Found: $N = 15 \cdot 4\%$; calculated for $C_{12}H_{14}N_2$, $N = 15 \cdot 1\%$.

2-Benzyl-5 : 6-dihydro-quinolo-1 : 3-diazole. (IV; $R = CH_2C_6H_5$.)

A mixture of 8-aminoquinoline (1·5 g.) and phenylacetic acid (2 g.) was gently fused over a free flame for thirty minutes until no further evolution of water occurred. The cooled melt was extracted with hydrochloric acid and the cleared acid solution basified with ammonia.

The oily base which separated soon solidified and was recrystallised from aqueous methyl alcohol. Colourless rhombs, m.p. 109°.

Found: N=11·2%; calculated for $C_{17}H_{16}N_2$, N=11·3%.

2-Hydroxymethyl-5 : 6-dihydro-quinolo-1 : 3-diazole. (V; R=H.)

A solution of 8-aminotetrahydroquinoline (1·5 g.) and glycollic acid (0·76 g.) in hydrochloric acid (4N; 10 c.c.) was gently refluxed for 35 minutes. On cooling and basifying with ammonia a white crystalline precipitate separated. After recrystallising from aqueous alcohol it formed faintly pink needles, m.p. 183°.

In a second experiment, 8-aminotetrahydroquinoline (5 g.) was gently heated with glycollic acid (2·5 g.) over a free flame until no more water was split out. The product was taken up in acid and recovered as above. Yield 2·5 grams.

Found: N=15·3%; calculated for $C_{11}H_{12}ON_2$, N=14·9%.

2-α-Hydroxyethyl-5 : 6-dihydro-quinolo-1 : 3-diazole. (V; R=CH_3.)

8-Aminotetrahydroquinoline (1·5 g.), lactic acid (0·9 g.) and hydrochloric acid (4N; 10 c.c.) were refluxed together for 35 minutes. The solution was then cooled and basified with ammonia. The pink solid which separated in poor yield was difficult to purify and gave solutions which assumed a deep red colour. It was finally recrystallised from dilute methyl alcohol and obtained in faintly pink rhombs, m.p. 142°. Better results were by refluxing 8-aminotetrahydroquinoline (2·5 g.) with lactic acid (20 g.) for two hours, pouring on to ice and basifying with ammonia. The almost colourless product (1·8 g.) was identified with the product obtained by Phillips's method, but it crystallised more easily and its solution became only faintly pink even on long standing.

Found: N=14·0%; calculated for $C_{12}H_{14}ON_2$, N=13·9%.

2-α-Hydroxybenzyl-5 : 6-dihydro-quinolo-1 : 3-diazole. (V; R=C_6H_5.)

A solution of dl-mandelic acid (1·5 g.) and 8-aminotetrahydroquinoline (1·5 g.) in hydrochloric acid (4N;

10 c.c.) was refluxed for 35 minutes, cooled and basified with ammonia. The separated crystalline base (1 g.) was recrystallised from alcohol and obtained in faintly pink rhombs, m.p. 205°.

Found: N=11·0%; calculated for $C_{17}H_{16}ON_2$, N=10·6%.

2-α-Hydroxybenzhydryl-5 : 6-dihydro-quinolo-1 : 3-diazole.

A mixture of 8-aminotetrahydroquinoline (1 g.) and benzilic acid (1·5 g.) was carefully heated over a free flame until evolution of water ceased. The cooled melt was taken up in, and recrystallised from, glacial acetic acid and obtained in colourless prisms melting at 275°.

Found: N=8·3%; calculated for $C_{23}H_{20}ON_2$, N=8·2%.

2-Methyl-3-keto-6 : 7-dihydroquinolo-1 : 4-diazine. (VIII.)

8-Aminotetrahydroquinoline (1 g.) was mixed with excess pyruvic acid (1 g.). Heat was evolved. Eventually after gentle warming ammonia was added, when the mass solidified. It was recrystallised from aqueous alcohol and obtained in colourless prisms melting at 113°.

Found: N=14·3%; calculated for $C_{12}H_{12}ON_2$, N=14·0%.

Ethyl β-(*8′-tetrahydroquinolylamino*) *crotonate.*

8-Aminotetrahydroquinoline (3 g.) was dissolved in ethyl acetoacetate (2·6 g.) and dilute hydrochloric acid (5N; 2 drops) added. Water soon commenced to separate. After 24 hours the oil was taken up and dried in ether and after removal of the solvent was left in a vacuum desiccator to crystallise. It was recrystallised from petroleum ether in which it is very soluble and obtained in fibrous needles, m.p. 56–57°.

Found: N=10·1%; calculated for $C_{15}H_{20}O_2N_2$, N=10·3%.

This substance is very soluble in all the usual organic solvents. When dropped into six times its weight of paraffin oil previously heated to 280° a vigorous reaction occurred, and on cooling the solution deposited colourless needles, which, after several recrystallisations from ligroin, melted at 128°.

Found: C=77·7, H=7·3, N=16·1%; calculated for $C_{11}H_{12}N_2$, C=76·7, H=7·0, N=16·2%.

A mixed melting point showed that this substance was identical with the 2-methyl-5 : 6-dihydro-quinolo-1 : 3-diazole described above.

dl-2 : 3-Diphenyl-6 : 7-dihydro-quinolo-1 : 4-diazine. (VI.)

A preliminary attempt to condense benzoin and 8-aminotetrahydroquinoline in alcoholic solution proved abortive. The condensation was best carried out as follows : Benzoin (2 g.) was fused with 8-aminotetrahydroquinoline (2 g.) and carefully heated over a free flame until no further water was evolved. The cooled melt was then recrystallised from alcohol and the base (2 g.) separated as orange plates which melt at 146°.

Found : N=9·0% ; calculated for $C_{23}H_{20}N_2$, N=9·0%.

Reaction of 8-Aminotetrahydroquinoline with Diacetyl.

Ice cold solutions of diacetyl (1 g.) in alcohol (5 c.c.) and 8-aminotetrahydroquinoline (2 g.) in alcohol (5 c.c.) were mixed and allowed to stand in ice for several hours. Pale yellow crystals (1 g.) separated. These were collected and recrystallised from a mixture of benzene and ligroin. Pale yellow prisms, m.p. 123°.

Found : C=76·3, H=7·7, N=16·1% ; calculated for $C_{22}H_{26}N_4$, C=76·3, H=7·5, N=16·1%.

This substance was not identical with the diazole (IV ; R=CH_3) described above. It appeared to be the anil formed from two molecules of base and one of diacetyl. Support for this view is to be found in the fact that unchanged diacetyl could be readily recovered from the reaction liquors in its preparation.

Condensation of 8-Aminotetrahydroquinoline with Alloxan.

(*a*) In the first experiments, 8-aminotetrahydroquinoline (0·5 g.) was dissolved in alcohol (20 c.c.) and a warm solution of anhydrous alloxan (0·5 g.) in alcohol (20 c.c.) added. A yellow precipitate which was practically insoluble in boiling alcohol, formed immediately. It was collected and recrystallised from glacial acetic acid, being obtained in lemon yellow needles, m.p. 255°.

Found : C=59·9, H=4·6, N=22·1% ; calculated for $C_{13}H_{10}O_2N_4$, C=61·4, H=4·0, N=22·0%.

(*b*) To a solution of 8-aminotetrahydroquinoline (1 g.) in glacial acetic acid (10 c.c.) containing boric acid (1 g.) was added a cooled solution of hydrated alloxan (2 g.) in glacial acetic acid (150 c.c.), the temperature being maintained at 20°. Almost immediately an orange precipitate commenced to form. [If the condensation was carried out at higher temperatures (e.g. 35°) the precipitate formed was always darker.] The product was almost insoluble in boiling alcohols, acetic acid, benzene, nitrobenzene and pyridine. A faint yellow colour and characteristic fluorescence indicated very slight solubility in alcohols. It dissolves in warm 15% hydrochloric acid solution to a pale yellow solution, which soon deposits yellow crystalline plates. The base can be regenerated in orange needles by addition of ammonia without delay to the filtered hydrochloric acid solution. It does not melt, or apparently alter below 320°.

Found : N = 22·0% ; calculated for $C_{13}H_{10}O_2N_4$, N=22·0%.

2-Methyl-4-hydroxy-1 : 10-phenanthroline. (XI.)

8-Aminoquinoline (10 g.) and ethyl acetoacetate (8 g.) were warmed together to a homogeneous melt, dilute (1 : 1) hydrochloric acid (3 drops) was added and the mixture was heated at 100° for ten hours. The oily product was taken up, washed and dried in ether, the solvent removed and the residue partially distilled *in vacuo* to remove unchanged acetoacetic ester and 8-aminoquinoline. The residual oil was poured into six times its weight of paraffin oil preheated to 270°. A vigorous reaction occurred and a solid crystallised. It was recrystallised from a mixture of benzene with a little absolute alcohol and was obtained in colourless prisms which softened at 183° and melted at 196°.

Found : N=13·1% ; calculated for $C_{13}H_{10}ON_2$, N=13·3%.

8-Acetoacetamidoquinoline.

Powdered 8-aminoquinoline (4 g.) was gradually added to ethyl acetoacetate (16 g.) maintained between 140° and 160°. Effervescence followed each addition and after heating for thirty minutes the mixture was allowed to cool. Ethyl alcohol was then added and crystallisation induced by scratching. The copious deposit was recrystallised from hot water, and obtained in colourless shining plates melting at 93°.

Found : N=12·3% ; calculated for $C_{13}H_{11}O_2N_2$, N=12·1%.

A dilute alcoholic solution of this substance gives intense red colours with ferric chloride solution or diazobenzene chloride solution. When attempts were made to effect its cyclisation with concentrated sulphuric acid to 2-hydroxy-4-methyl-1 : 10-phenanthroline the substance was either recovered unchanged (cold sulphuric acid) or was hydrolysed to 8-aminoquinoline (hot sulphuric acid). No trace of phenanthroline derivative could be obtained.

β-(*8′-Quinolyamino*)-*propenyl Methyl Ketone.*

8-Aminoquinoline (14·4 g.) and acetylacetone (10 g.) were heated together at 100° for two hours. Water separated. The resulting oil soon crystallised to a solid cake (yield practically quantitative), and this was taken up in hot alcohol. After filtering and cooling the solid separated in magnificent colourless prisms melting at 95°.

Found: $C=74{\cdot}1$, $H=6{\cdot}4$, $N=12{\cdot}6\%$; calculated for $C_{14}H_{14}ON_2$, $C=74{\cdot}3$, $H=6{\cdot}2$, $N=12{\cdot}4\%$.

Attempts to cyclise this derivative to a phenanthroline were unsuccessful. It became bright orange on contact with cold concentrated sulphuric acid, and dissolved to a yellowish brown solution with slight heat evolution. It was not possible to recover any product other than 8-aminoquinoline from the sulphuric acid solution, even after several hours' heating. Attempts to effect the cyclisation with phosphoric anhydride or phosphorus oxychloride were equally fruitless.

7-Hydroxy-9-methyl-4 : 10-phenanthroline. (XII.)

5-Aminoquinoline (5·6 g.) and ethyl acetoacetate (5·2 g.) were warmed together, dilute (1 : 1) hydrochloric acid (2 drops) added, and the mixture heated at 100° for three hours. The oil was then washed and dried in ether, and after removal of the solvent was poured into paraffin oil (60 g.) preheated to 270°. There was a vigorous reaction and pale yellow plates commenced to separate almost at once. They were collected and eventually recrystallised from boiling nitrobenzene, being practically insoluble in all the usual organic solvents. The substance appeared to alter slightly at 300° when heated, but did not melt below 345°.

Found: $C=72{\cdot}9$, $H=4{\cdot}6$, $N=13{\cdot}4\%$; calculated for $C_{13}H_{10}ON_2$, $C=74{\cdot}3$, $H=4{\cdot}8$, $N=13{\cdot}3\%$.

Condensation of 5-Aminoquinoline with Ethyl cyclohexanone-2-carboxylate.

5-Aminoquinoline (4·3 g.) and ethyl cyclohexanone-2-carboxylate (5·1 g.) were warmed together, dilute (1 : 1) hydrochloric acid (2 drops) added, and the mixture heated at 100° for seven hours. The resultant oily mixture was poured into paraffin oil (50 g.) previously heated to 280°. A gummy mass separated which was recrystallised from much methyl alcohol. Colourless rhombs commencing to decompose at 250°, but not completely melted below 300°, were obtained.

Found: N=11·0%; calculated for $C_{16}H_{14}ON_2$, N=11·2%.

This substance thus appears to be the expected acridine derivative 7-hydroxy-8 : 9 : 10 : 11-tetrahydro-8 : 9-benz-4 : 10-phenanthroline—better named perhaps as 7-hydroxy—4 : 12-acridinoline.

It was impossible to isolate any similar product by reacting 8-aminoquinoline and ethyl cyclohexanone-2-carboxylate together.

8-Chloracetylaminoquinoline. (XIV.)

A solution of chloracetyl chloride (4 g.) and chloroform (10 c.c.) were gradually added with vigorous agitation to a solution of 8-aminoquinoline in ice-cold chloroform (20 c.c.). The mixture became orange in colour and very soon deposited a yellow crystalline solid. Eventually the chloroform suspension was shaken out with sodium bicarbonate solution several times, the chloroform layer separated, dried, and then partially evaporated. Colourless needles (4·5 g.) deposited. After recrystallisation from methyl alcohol they melted at 132°, and the melt turned yellow at a slightly higher temperature.

Found: N=13·3%; calculated for $C_{11}H_9ON_2Cl$, N=12·7%.

Anhydroglycollylaminoquinolinium chloride.

8-Chloracetylaminoquinoline (3 g.) was heated to 200° in a paraffin bath for 15 minutes. The mass turned orange brown in colour. After cooling this was extracted with water (40 c.c.) and to the cooled filtered extract ethyl alcohol (200 c.c.) was added.

The quaternary ammonium chloride came down from this solvent as a yellow powder on addition of ether.

This quaternary ammonium salt is readily soluble in water but only sparingly so in alcohol. Its aqueous solution gives an immediate precipitate of silver chloride when treated with cold silver nitrate solution containing nitric acid.

ACKNOWLEDGMENTS.

The authors gratefully acknowledge the receipt of a grant from the Commonwealth Government Research Fund, which has materially assisted the publication of the results recorded above.

Department of Organic Chemistry,
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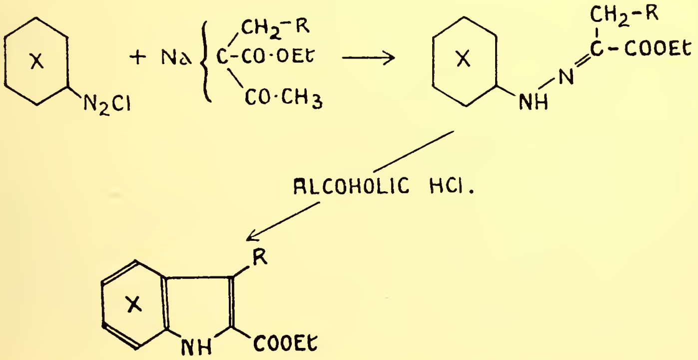
RESEARCHES ON INDOLES.*

PART IV.—THE UTILISATION OF THE JAPP-KLINGEMANN REACTION FOR THE PREPARATION OF SUBSTITUTED INDOLE CARBOXYLIC ACIDS.

By GORDON K. HUGHES, B.Sc.,
and FRANCIS LIONS, B.Sc., Ph.D.

(*Manuscript received, November 17, 1937. Read, December 1, 1937.*)

Perkin and Weizmann (*J.C.S.*, 1906, 1649) recorded a description of several benzophenone derivatives which were mostly prepared by students in the laboratories of the University of Manchester; they commented on the desirability of allotting relatively simple investigations to senior students, both for the arousing of interest and enthusiasm, and also for the introduction to methods of research and the creation of a desire for further inquiry and original work. In this paper there are described several derivatives of indole which have all been prepared by students of organic chemistry in their final (pass) year at this University. The Japp-Klingemann reaction (*Berichte*, 1888, *21*, 549; *Annalen*, 1888, *247*, 218) has been utilised in each instance for the preparation of the necessary intermediate substituted phenylhydrazones of α-keto esters, starting from the sodio-derivatives of α-mono-alkylated-β-keto esters and aryldiazonium chlorides: and these have then been cyclised to the corresponding substituted indole α-carboxylic esters by means of alcoholic hydrogen chloride, according to the scheme



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* For Part III, see THIS JOURNAL, 1932, *66*, 516.

From the indole esters the corresponding indole acids were then prepared by hydrolysis.

Four substituted β-keto esters have been utilised, viz.: ethyl α-acetylpropionate (I), ethyl α-acetylbutyrate (II), ethyl α-acetylcaproate (III) and ethyl α-acetyl-β-phenyl propionate (IV); and these have been combined with the diazonium chlorides from the following aromatic bases: α-naphthylamine (V), β-naphthylamine (VI), o-phenetidine (VII), p-phenetidine (VIII), p-anisidine (IX), p-bromaniline (X), ethyl p-aminobenzoate (XI).

The use of meta substituted arylamines was avoided because it was not considered desirable with such junior investigators to encounter the possibility of formation of 5- and 7-substituted indoles, or a mixture of these, with the consequent difficulties of separation and orientation. Two failures to effect cyclisation of the intermediate phenylhydrazones to indoles were reported in spite of repeated attempts, namely that of p-carbethoxy-phenylhydrazone of ethyl pyruvate, and that of the p-carbethoxy-phenylhydrazone of ethyl α-ketobutyrate. It is worthy of comment that the Fischer indole synthesis apparently experiences little difficulty when ortho or para alkoxylated phenylhydrazones are submitted to acid treatment, although, it will be recalled, the Combes quinoline synthesis fails completely with ortho and para anisidines and phenetidines (cf. Roberts and Turner, *J.C.S.*, 1927, 1832). Apparently the opposition of an alkyloxy group to the entrance of a substituent in the meta position of a benzene ring is not sufficiently powerful to prevent indole ring closure in that position.

Experimental.

In all experiments freshly purified amines and esters were used.

Formation of Substituted Phenylhydrazones.

An ice cold solution of potassium hydroxide (17 c.c. of a 50% solution) was added with vigorous stirring to an ice-cold solution of the ester (1/20th gram molecule) in absolute alcohol (50 c.c.). Ice water (100 c.c.) was then added, followed without delay by a solution of the substituted benzene diazonium chloride [from amine (1/20th molecule), concentrated hydrochloric acid (20 c.c.), water (30 c.c.), and sodium nitrite (3·5 g.)] which had been cooled to —5°.

The mixture was kept vigorously stirred for a further five minutes, after which the hydrazone which separated as a red-brown oil was extracted three times with ether. The combined ether extracts were washed twice with 5% caustic soda solution and then thoroughly washed with water, and the solvent removed.

If the hydrazone crystallised at this stage, it was purified for analysis by recrystallisation from a suitable solvent.

Cyclisation and Formation of Indole Esters.

The crude hydrazone was dissolved in dry alcohol (60 c.c.) and dry hydrogen chloride was passed until ammonium chloride was precipitated (30–180 minutes). After standing for a further two hours the solution was poured into ice water and the crude indole carboxylic ester separated by filtration if solid, or extraction with ether if liquid.

The method of purification adopted is shown for each substance. Each was recrystallised to constant melting point, as many as seven recrystallisations being carried out in certain instances.

Hydrolysis and Formation of Indole Carboxylic Acids.

For the hydrolysis of the esters to the corresponding acids the filtrates from the various recrystallisations were evaporated to dryness, the residue taken up in alcohol and refluxed for two hours with an excess of potassium hydroxide. Most of the alcohol was then removed before precipitation of the indole acid with dilute hydrochloric acid and recrystallisation from a suitable solvent.

With J. G. McKEAN AND A. J. MURRAY.

The base used was α-naphthylamine.

α-Naphthylhydrazone of ethyl pyruvate.

From (I) and (V). Recrystallised from alcohol (charcoal) as orange platelets m.p. 125°.

Found: N=10·8%; calculated for $C_{15}H_{16}N_2O_2$, N=10·9%.

Ethyl-6 : 7-benzindole-8-carboxylate.

Repeatedly recrystallised from ethyl alcohol (charcoal) as a light brown powder, m.p. 170°.

Found: C=74·9, H=5·3%; calculated for $C_{15}H_{13}NO_2$, C=75·3, H=5·4%.

6 : 7-Benzindole-8-carboxylic acid.

Recrystallised several times from benzene (charcoal) as a light brown powder, m.p. 204–205°.

Found : $C=72 \cdot 9$, $H=4 \cdot 5\%$; calculated for $C_{13}H_9NO_2$, $C=73 \cdot 9$, $H=4 \cdot 3\%$.

Ethyl 7-Methyl-6 : 7-benzindole-8-carboxylate.

From (II) and (V). Recrystallised several times from alcohol (charcoal) as pale yellow powder, m.p. 176°.

Found : $C=76 \cdot 0$, $H=6 \cdot 3\%$; calculated for $C_{16}H_{15}NO_2$, $C=75 \cdot 9$, $H=5 \cdot 9\%$.

Ethyl-7-n-propyl-5 : 6-benzindole-8-carboxylate.

From (III) and (V). After repeated recrystallisation from alcohol (charcoal) it was obtained as pale pink needles, m.p. 185–186°.

Found : $C=77 \cdot 0$, $H=6 \cdot 3\%$; calculated for $C_{18}H_{19}NO_2$, $C=76 \cdot 9$, $H=6 \cdot 8\%$.

7-n-Propyl-5 : 6-benzindole-8-carboxylic acid.

Recrystallised from benzene (charcoal) as a pale pink powder, m.p. 182–183°.

Found : $C=76 \cdot 1$, $H=5 \cdot 9\%$; calculated for $C_{16}H_{15}NO_2$, $C=75 \cdot 9$, $H=5 \cdot 9\%$.

Ethyl 7-phenyl-5 : 6-benzindole-8-carboxylate.

From (IV) and (V). Recrystallised from benzene (charcoal) as orange needles, m.p. 187°.

Found : $C=79 \cdot 3$, $H=5 \cdot 6\%$; calculated for $C_{21}H_{17}NO_2$, $C=80 \cdot 0$, $H=5 \cdot 4\%$.

With V. CALLANAN AND D. H. FREEMAN.

The base used was β-naphthylamine (VI).

Ethyl 4 : 5-benzindole-2-carboxylate.

From (I) and (VI). Recrystallised from petroleum ether as white needles, m.p. 161°.

Found : $C=75 \cdot 5$, $H=5 \cdot 7\%$; calculated for $C_{15}H_{13}NO_2$, $C=75 \cdot 3$, $H=5 \cdot 4\%$.

4 : 5-Benzindole-2-carboxylic acid.

Recrystallised from aqueous methyl alcohol (charcoal) as pale yellow needles, m.p. 160°.

Found : C=74·2, H=4·2% ; calculated for $C_{13}H_9NO_2$, C=73·9, H=4·3%.

Ethyl-1-methyl-4 : 5-benzindole-2-carboxylate.

From (II) and (VI). Extracted with petroleum ether followed by recrystallisation from ethyl alcohol (charcoal) as pale pink needles, m.p. 176°.

Found : C=75·9, H=6·2% ; calculated for $C_{16}H_{15}NO_2$, C=75·9, H=5·9%.

1-Methyl-4 : 5-benzindole-2-carboxylic acid.

Recrystallised from methyl alcohol as a white powder, m.p. 176°.

Found : C=75·3, H=4·7% ; calculated for $C_{14}H_{11}NO_2$, C=74·7, H=4·9%.

Ethyl 1-Phenyl-4 : 5-benzindole-2-carboxylate.

From (IV) and (VI). Recrystallised four times from alcohol (charcoal) as pale pink needles, m.p. 179°.

Found : C=79·7, H=5·1% ; calculated for $C_{21}H_{17}NO_2$, C=80·0, H=5·4%.

1-Phenyl-4 : 5-benzindole-2-carboxylic acid.

Recrystallised from aqueous methyl alcohol (charcoal) as creamy needles, m.p. 201°.

Found : C=79·8, H=4·3% ; calculated for $C_{19}H_{13}NO_2$, C=79·4, H=4·5%.

With C. S. RALPH AND R. RASSACK.

The base was o-phenetidine (VII).

Ethyl-7-ethoxyindole-2-carboxylate.

From (I) and (VII). Distilled under reduced pressure at 170–175°/2 mm. Solidified on cooling and recrystallised from alcohol as almost colourless needles, m.p. 160°.

Found : C=66·6, H=6·2% ; calculated for $C_{13}H_{15}NO_3$, C=67·0, H=6·4%.

Ethyl-3-n-propyl-7-ethoxy-indole-2-carboxylate.

From (III) and (VII). Distilled under reduced pressure at 177°/2 mm. Would not solidify even after long standing.

Found: C=69·1, H=7·7%; calculated for $C_{16}H_{21}NO_3$, C=69·9, H=7·6%.

3-n-Propyl-7-ethoxy-indole-2-carboxylic acid.

Recrystallised from aqueous alcohol as white needles, m.p. 162°.

Found: C=67·8, H=6·8%; calculated for $C_{14}H_{17}O_3N$, C=68·0, H=6·9%.

Ethyl-3-phenyl-7-ethoxy-indole-2-carboxylate.

From (IV) and (VII). Distilled under reduced pressure, the fraction boiling at 216–224°/2 mm. being collected. Solidified on standing and was recrystallised from alcohol as white needles, m.p. 93°.

Found: C=73·6, H=6·0%; calculated for $C_{19}H_{19}NO_3$, C=73·8, H=6·1%.

3-Phenyl-7-ethoxy-indole-2-carboxylic acid.

Recrystallised from alcohol as pale yellow needles, m.p. 206–207°.

Found: C=72·3, H=5·3%; calculated for $C_{17}H_{15}NO_3$, C=72·6, H=5·3%.

With J. DOMBROSKI AND F. FINCH.

The base used was p-phenetidine (VIII).

Ethyl 5-ethoxy-indole-2-carboxylate.

From (I) and (VIII). Recrystallised from alcohol as almost colourless needles, m.p. 155–6°.

Found: C=66·7, H=6·3%; calculated for $C_{13}H_{15}O_3N$, C=67·0, H=6·4%.

Ethyl-3-methyl-5-ethoxy-indole-2-carboxylate.

From (II) and (VIII). Repeatedly recrystallised from alcohol (charcoal) as pale yellow needles, m.p. 167°.

Found: C=68·2, H=7·0%; calculated for $C_{14}H_{17}O_3N$, C=68·0, H=6·9%.

3-Methyl-5-ethoxy-indole-2-carboxylic acid.

Recrystallised from dilute alcohol as pale yellow needles, m.p. 178°.

Found : C=66·3, H=6·0% ; calculated for $C_{12}H_{13}O_3N$, C=65·8, H=5·9%.

Ethyl-3-n-propyl-5-ethoxy-indole-2-carboxylate.

From (III) and (VIII). Recrystallised three times from alcohol, m.p. 142°.

Found : C=70·1, H=7·4% ; calculated for $C_{16}H_{21}O_3N$, C=69·9, H=7·6%.

3-n-Propyl-5-ethoxy-indole-2-carboxylic acid.

Recrystallised twice from 50% alcohol as a white powder, m.p. 178°.

Found : C=67·7, H=7·4% ; calculated for $C_{14}H_{17}O_3N$, C=68·0, H=6·9%.

Ethyl-3-phenyl-5-ethoxy-indole-2-carboxylate.

From (IV) and (VIII). Recrystallised from alcohol (charcoal) as almost colourless needles, m.p. 148–149°.

Found : C=73·6, H=6·4% ; calculated for $C_{19}H_{19}NO_3$, C=73·8, H=6·1%.

3-Phenyl-5-ethoxy-indole-2-carboxylic acid.

Recrystallised from 50% alcohol as light brown powder, m.p. 183–5°.

Found : C=73·0, H=5·2% ; calculated for $C_{17}H_{15}NO_3$, C=72·6, H=5·3%.

With R. ANDREWS AND R. C. BETTY.

The amine used was p-anisidine (IX).

Ethyl-5-methoxy-indole-2-carboxylate.

From (I) and (IX). Recrystallised from petroleum ether (60–80°) with charcoal and finally from alcohol as white needles, m.p. 152–153°.

Found : C=66·0, H=6·0% ; calculated for $C_{12}H_{13}NO_3$, C=65·8, H=5·9%.

Ethyl-3-methyl-5-methoxy-indole-2-carboxylate.

From (II) and (IX). Recrystallised from petroleum ether (charcoal) and finally from alcohol, m.p. 146–147°.

Found : C=67·2, H=6·4% ; calculated for $C_{13}H_{15}NO_3$, C=67·0, H=6·4%.

Ethyl-3-n-propyl-5-methoxy-indole-2-carboxylate.

From (III) and (IX). Solidified after treatment with petroleum ether (charcoal) and was recrystallised several times from alcohol as small white needles, m.p. 106°.

Found : C=69·1, H=7·3% ; calculated for $C_{15}H_{19}NO_3$, C=69·0, H=7·3%.

Ethyl-2-phenyl-5-methoxy-indole-2-carboxylate.

From (IV) and (IX). First recrystallised from petroleum ether followed by alcohol as a grey powder, m.p. 121–122°.

Found : C=73·0, H=5·6% ; calculated for $C_{18}H_{17}NO_3$, C=73·2, H=5·8%.

With R. H. SCOTT AND C. W. VERNON.

Base used was p-bromaniline (X).

Ethyl-5-bromo-indole-2-carboxylate.

From (I) and (X). Recrystallised seven times from aqueous alcohol (charcoal) as very pale yellow needles, m.p. 153°.

Found : C=47·8, H=3·9% ; calculated for $C_{11}H_{10}NO_2Br$, C=49·3, H=3·7%.

5-Bromo-indole-2-carboxylic acid.

Recrystallised several times from aqueous alcohol and finally from benzene as white needles. Melts with decomposition at 188°.

Found : C=45·5, H=2·7% ; calculated for $C_9H_6NO_2Br$, C=45·0, H=2·5%.

Ethyl-3-methyl-5-bromo-indole-2-carboxylate.

From (II) and (X). Recrystallised eight times from aqueous alcohol (charcoal) as canary yellow crystals, m.p. 163°.

Found : C=50·7, H=4·5% ; calculated for $C_{12}H_{12}NO_2Br$, C=51·1, H=4·3%.

3-Methyl-5-bromo-indole-2-carboxylic acid.

Recrystallised from aqueous alcohol as white needles, m.p. 217–218°.

Found: C=47·5, H=3·5%; calculated for $C_{10}H_8NO_2Br$, C=47·2, H=3·2%.

Ethyl-3-n-propyl-5-bromo-indole-2-carboxylate.

From (III) and (X). Recrystallised several times from alcohol as pale pink needles, m.p. 149°.

Found: C=54·0, H=5·1%; calculated for $C_{14}H_{16}NO_2Br$, C=54·2, H=5·2%.

3-n-Propyl-5-bromo-indole-2-carboxylic acid.

Recrystallised from alcohol (charcoal) as white powder, m.p. 160°.

Found: C=50·9, H=4·2%; calculated for $C_{12}H_{12}NO_2Br$, C=51·1, H=4·3%.

Ethyl-3-phenyl-5-bromo-indole-2-carboxylate.

From (IV) and (X). Recrystallised from alcohol as white needles, m.p. 185°.

Found: C=60·1, H=4·1%; calculated for $C_{17}H_{14}NO_2Br$, C=59·3, H=4·1%.

3-Phenyl-5-bromo-indole-2-carboxylic acid.

Recrystallised from benzene as a white powder, m.p. 216°.

Found: C=57·2, H=3·0%; calculated for $C_{15}H_{10}NO_2Br$, C=57·0, H=3·2%.

With A. FLACK AND C. H. LAURENCE.

The base used was ethyl p-aminobenzoate (XI).

Ethylpyruvate p-carbethoxyphenylhydrazone.

From (I) and (XI). Recrystallised from benzene and petroleum ether as lustrous white plates, m.p. 137°.

Found: C=60·2, H=6·3, N=10·3%; calculated for $C_{14}H_{18}N_2O_4$, C=60·4, H=6·5, N=10·1%.

The hydrazone was unaffected by the hydrogen chloride treatment and also by boiling with acetic acid for some hours.

Ethyl α-ketobutyrate p-carbethoxyphenylhydrazone.

From (II) and (XI). Recrystallised from benzene and petroleum ether as white glistening plates, m.p. 141°.

Found: N=9·8%; calculated for $C_{15}H_{20}N_2O_4$, N=9·6%.

Ethyl-3-methyl-5-carbethoxy-indole-2-carboxylate.

From hydrazone of (II) and (XI). Recrystallised from benzene-petroleum ether as white needles, m.p. 181°.

Found: C=65·1, H=6·2%; calculated for $C_{15}H_{17}NO_4$, C=65·4, H=6·1%.

3-Methyl-indole-2 : 5-dicarboxylic acid.

The hydrolysis eliminated both ethyl groups. Recrystallised from aqueous alcohol (charcoal) as a white powder, m.p. 298°.

Found: C=59·4, H=4·0%; calculated for $C_{11}H_9NO_4$, C=60·3, H=4·1%.

Diethyl-3-n-propyl-indole-2 : 5-dicarboxylate.

From (III) and (XI). Recrystallised from alcohol as pale yellow prisms, m.p. 133–134°.

Found: C=67·7, H=6·4%; calculated for $C_{17}H_{21}NO_4$, C=67·3, H=7·0%.

3-n-Propyl-indole-2 : 5-dicarboxylic acid.

Recrystallised from methyl alcohol as a white powder, m.p. 282°.

Found: C=62·4, H=5·3%; calculated for $C_{13}H_{13}NO_4$, C=63·2, H=5·3%.

Diethyl-3-phenyl-indole-2 : 5-dicarboxylate.

From (IV) and (XI). Crude yield, 13 grams. Recrystallised from alcohol (charcoal) as pale yellow needles, m.p. 196–197°.

Found: C=71·2, H=5·7%; calculated for $C_{20}H_{19}NO_4$, C=71·2, H=5·7%.

3-Phenyl-indole-2 : 5-dicarboxylic acid.

Recrystallised from alcohol as a pale yellow powder, sinters at 270°, melting sharply at 290°.

Found: C=67·8, H=4·3%; calculated for $C_{16}H_{11}NO_4$, C=68·3, H=3·9%.

ACKNOWLEDGMENTS.

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RESEARCHES ON INDOLES.

PART V.—COUMARONO (3, 2-b) INDOLE AND DERIVATIVES.

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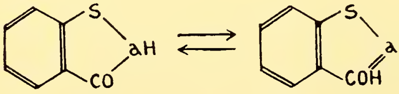
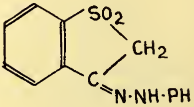
FRANCIS LIONS, B.Sc., Ph.D.,
and RITA HARRIET HARRADENCE, B.Sc.

(*Manuscript received, November 17, 1937. Read, December 1, 1937.*)

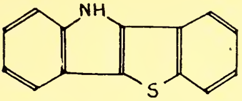
Robinson and Robinson (*J.C.S.*, 1918, 639) have discussed the conditions necessary for the success of Fischer's indole synthesis (E. Fischer, *Annalen*, 1886, *236*, 126) and have pointed out that " aldehydes and ketones, which are readily changed to enols, might be expected to give phenylhydrazones readily convertible to indoles ". They adduced evidence in favour of this contention, and their views can hardly be considered other than correct. McClelland and D'Silva (*J.C.S.*, 1932, 227), in a study of the indole cyclisation of the phenylhydrazones of 3-oxythionaphthenes, pointed out that " oxidation of the sulphur to the sulphone condition in a cyclic system of the type (I) appears to restrain the tendency to enolisation. Hence, the phenylhydrazone of 3-oxy-1-thionaphthene (I ; a=CH), in contrast to the phenylhydrazone (II) derived from the corresponding dioxide, might be expected to undergo the indole transformation readily ". Experimental work then proved the accuracy of McClelland's and D'Silva's contention, a series of derivatives of thionaphthindole (III) being readily prepared, whilst (II) could not be cyclised to an indole.



I.

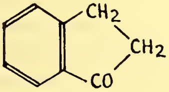


II.

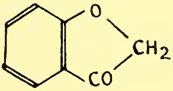


III.

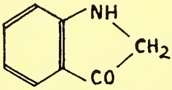
The reactivity of the keto methylene system in 3-oxy-1-thionaphthene is paralleled by that of similar keto methylene systems in substances such as α-hydrindone (IV), and heterocyclics such as coumaranone (V) and indoxyl (VI). Thus, (I) (a=CH), (IV), (V) and (VI) all condense readily with aldehydes to form products of the "indogenide" type. Also Armit and Robinson (*J.C.S.*, 1922, 827) have shown that the phenylhydrazones of α-hydrindone and β-hydrindone readily undergo the Fischer synthesis, with formation of the corresponding indeno-indoles. It might, therefore, be anticipated that the phenylhydrazones of (V) and (VI) may be readily cyclised to indole. Further supporting evidence for this view is to be found in the observations of Robinson and Thornley (*J.C.S.*, 1926, 3144), who showed that the phenylhydrazones of ω-methoxyacetophenone and ω-benzoylaminoacetophenone are easily cyclised in boiling glacial acetic acid to 2-phenyl-3-methoxyindole and 2-phenyl-3-benzoylaminoindole respectively.



IV.

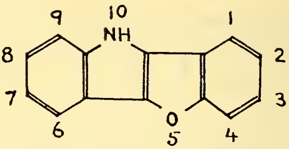


V.



VI.

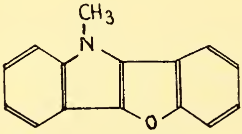
Experiments on the preparation and treatment with acid of various arylhydrazones of coumaranone (V) have been carried out. As was anticipated the corresponding coumaronoindoles were formed with great ease. Thus, warming together of coumaranone and phenylhydrazine leads to rapid elimination of water, and formation of coumaranone phenylhydrazone, an oily substance which passes over into coumarono (3, 2-b) indole (VII) at once on boiling with glacial acetic acid. In a similar way, p-tolyl hydrazine can be condensed with coumaranone, and the product readily cyclised in glacial acetic acid to 7-methyl coumarono (3, 2-b) indole which melts at 183°; β-naphthyl hydrazine gives 6 : 7-benzcoumarono (3, 2-b) indole, a beautifully crystalline substance melting at



VII.

166°; and p-bromophenylhydrazine yields 7-bromo-coumarono (3, 2-b) indole, a colourless crystalline substance melting at 159°. With asymmetrical methyl phenyl-hydrazine, coumaranone reacts very vigorously and it is possible to isolate 10-methyl coumarono-(3, 2-b) indole (VIII) as a pale brown substance melting at 240°.

From these experiments it is clear that the readily enolisable ketone coumaranone behaves in the Fischer synthesis exactly as might be expected. It became of interest, therefore, to examine whether the azine of coumaranone would eliminate ammonia and undergo cyclisation to the dicoumaronopyrrole (IX) when treated with acid reagents, in the same way that the azine of desoxybenzoin is converted into tetraphenylpyrrole (Robinson and Robinson, *loc. cit.*). Both coumaranone and desoxybenzoin contain isolated keto methylene systems



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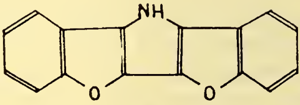
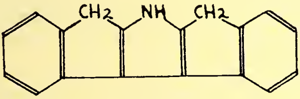


IX.

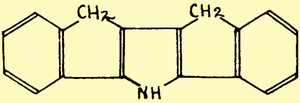
and there is no possibility of abnormality with the azine reaction as in the case of cyclohexanone (cf. Perkin and Plant, *J.C.S.*, 1924, 1503; Plant, *J.C.S.*, 1930, 1595).

Coumaranone readily forms an azine when treated with hydrazine acetate. It is a pale yellowish-green, crystalline substance melting at 207–8° and eliminates ammonia with surprising ease. Mere boiling of a solution of the azine in glacial acetic acid for several minutes is sufficient, and the dicoumaronopyrrole soon crystallises in dark green gleaming plates which melt at 330°.

In view of this success it was decided to examine the reaction with α-hydrindone and β-hydrindone. Consideration of the formulæ of these substances at once suggests that β-hydrindone, which has methylene groups between a benzene nucleus and a carbonyl group, should be a more readily enolisable ketone than α-hydrindone, and in consequence should yield an azine which would be much more easily converted to a diindenopyrrole (X) than the azine from α-hydrindone. It is merely necessary to treat β-hydrindone azine with 5% methyl or ethyl alcoholic hydrogen chloride in the cold, to pass dry hydrogen chloride into an ethereal or alcoholic suspension, or to boil it with glacial acetic acid for a few minutes to convert it to the pyrrole (X). On the other hand α-hydrindone azine only gives the pyrrole (XI) when dry hydrogen chloride is passed over the fused material at about 170°.



X.



XI.

We propose to continue this investigation and to apply the azine reaction to 3-oxythionaphthene and indoxyl, and also to examine the Fischer synthesis with indoxyl and substituted indoxyls.

Experimental.

Coumaranone.

Two main methods are available for the synthesis of coumaranone: (*a*) cyclisation of phenoxyacetyl chloride with anhydrous aluminium chloride (cf. e.g. Higginbotham and Stephen, *J.C.S.*, 1920, 1534); and (*b*) application of the Fries reaction to phenyl chloracetate followed by separation of the o-chloracetyl phenol and treatment of this with alcoholic sodium acetate (cf. Fries and Pfaffendorf, *Berichte*, 1910, *43*, 214). An excellent review of both methods, with suggested improvements is given by Mameli (*Gazzetta chim. Ital.*, 1926, *56*, 759). In our experience, method (*a*) is unsuitable for large scale preparations, whilst by method (*b*) it was readily possible to prepare 50 grams of coumaranone from 160 grams of phenol.

Coumarono-(3, 2-b)-indole (VII).

Phenylhydrazine (3·6 g.) and coumaranone (4·5 g.) were heated together on the water-bath, whereby water was split out with formation of a gummy phenylhydrazone. This was dissolved in about ten times its weight of glacial acetic acid and heated for a few minutes at the boiling point. The solution became dark green and on cooling and standing a crystalline solid separated. Filtered off, dried and recrystallised from much petroleum ether it formed colourless platelets, m.p. 198°. About 1 g. of substance is obtained in this way, but the acetic acid mother-liquors contain the bulk of the yield, which may be recovered by careful precipitation with water, and recrystallisation of the product from petroleum ether.

Found: $C=80 \cdot 7$, $H=4 \cdot 4\%$; calculated for $C_{14}H_9ON$, $C=81 \cdot 2$, $H=4 \cdot 3\%$.

7-Methyl-coumarono-(3, 2-b)-indole.

This substance was prepared from coumaranone (2·6 g.) and p-tolylhydrazine (2·4 g.) using the same method as in the preparation of 2 : 3-coumarono-indole. Recrystallised from petroleum ether the product formed colourless glistening plates, m.p. 183°.

Found: $C=81 \cdot 5$, $H=4 \cdot 6\%$; calculated for $C_{15}H_{11}ON$, $C=81 \cdot 4$, $H=5 \cdot 0\%$.

7-Bromo-coumarono-(3, 2-b)-indole.

A solution of coumaranone (2·7 g.) and p-bromophenylhydrazine (3·75 g.) in glacial acetic acid (30 c.c.) was boiled gently for fifteen minutes. Water (10 c.c.) was then carefully added and the mixture set aside. On cooling most of the indole crystallised as a dirty dark green powder, which was collected, washed, dried and extracted with much hot petroleum ether. The indole crystallised from the concentrated filtered extract in gleaming colourless plates melting at 159°.

Found: $C=58 \cdot 5$, $H=2 \cdot 9\%$; calculated for $C_{14}H_8ONBr$, $C=58 \cdot 7$, $H=2 \cdot 8\%$.

6 : 7-Benz-coumarono (3, 2-b)-indole (VIII).

Coumaranone (4·5 g.) and β-naphthylhydrazine hydrochloride (6·5 g.) were heated on the water-bath with a slight excess of crystalline sodium acetate (5 g.) and sufficient glacial acetic acid to keep the reactants in solution. After two hours a little water was added and the solution cooled. A brown solid deposit was formed, which was collected and crystallised twice from benzene. In this way colourless needles, m.p. 166°, were obtained.

Found: C=83·9, H=4·4%; calculated for $C_{18}H_{11}ON$, C=84·1, H=4·3%.

10-Methyl-coumarono (3, 2-b)-indole.

Coumaranone (1·3 g.) was added to as-phenylmethylhydrazine (1·2 g.) in glacial acetic acid (5 c.c.). A vigorous reaction set in and the liquid momentarily boiled. When the reaction had subsided the mixture was heated for a short time on the water-bath, then allowed to stand for two days. At the end of this time a small quantity of crystals had separated. These were collected and washed with a little acetic acid. Yield, 75 mg. The product formed brownish plates, m.p. 240°.

Found: C=81·4, H=4·4%; calculated for $C_{15}H_{11}ON$, C=81·4, H=5·0%.

Coumaranone azine.

A solution of hydrazine sulphate (2·7 g.) and sodium acetate (9 g.) in water (80 c.c.) was added to a solution of coumaranone (4·5 g.) in alcohol (160 c.c.) and the solution heated under reflux for two hours. The azine was collected after cooling, and was obtained pure after two recrystallisations from ethyl acetate in pale greenish yellow needles melting at 207–8°.

Found: N=10·6%; calculated for $C_{16}H_{12}O_2N_2$, N=10·7%.

This azine resists hydrolysis by methyl alcoholic hydrochloric acid, but is hydrolysed by boiling for several minutes with strong aqueous hydrochloric acid solution.

Dicoumaronopyrrole. (IX.)

Coumaranone-azine (1 g.) was dissolved in glacial acetic acid (10 c.c.) and the solution boiled for several minutes. A dark green colour developed and a crystalline solid commenced to separate. After cooling and standing the crystals were collected. They were dark green in colour, and melted at 330°.

Found: N=5·9%; calculated for $C_{16}H_9O_2N$, N=5·7%.

β-*Hydrindone azine.*

β-Hydrindone (5 g.) was dissolved in alcohol and an excess of hydrazine hydrate (12 g. of 50% solution) added.

There was no apparent reaction until after the addition of a few drops of acetic acid, when the azine commenced to separate at once as a white precipitate. It was collected after fifteen hours' standing, and became pink in colour on exposure to air (yield, 4·8 g.). It could be recrystallised from boiling benzene or dioxan, in both of which it is sparingly soluble, and was thus obtained in bright red crystals melting at 195–196°.

Found : $N=10 \cdot 5\%$; calculated for $C_{18}H_{16}N_2$, $N=10 \cdot 8\%$.

2 : 1 : 2′ : 1′-Di-indenopyrrole (*2 : 3 : 4 : 5*). (X.)

β-Hydrindone azine can be cyclised to the corresponding di-indenopyrrole with extreme ease under very mild conditions. Cyclisation can be accomplished by treatment with 5% methyl or ethyl alcoholic hydrogen chloride in the cold or on warming, by passing dry hydrogen chloride into an ethereal or alcoholic suspension, or by boiling with glacial acetic acid.

β-Hydrindone azine was treated with an excess of 5% methyl alcoholic hydrogen chloride and warmed on the water-bath for five minutes. It dissolved to a dark brown solution ; on evaporating a small portion of this solution a white precipitate of ammonium chloride appeared, and on boiling with sodium hydroxide the odour of ammonia was observed. From the brown solution water precipitated a yellowish brown solid, the colour of which changed to olive green on treatment with alkali. The product was insoluble in most organic solvents but dissolved readily in the cold in glacial acetic acid or pyridine. It can be recrystallised from aqueous pyridine, but the product appears amorphous. It does not melt below 360°.

Found : $N=5 \cdot 7\%$; calculated for $C_{18}H_{13}N$, $N=5 \cdot 7\%$.

1 : 2 : 1′ : 2′-Di-indeno pyrrole (*2 : 3 : 4 : 5*). (XI.)

α-Hydrindone azine (Revis and Kipping, *J.C.S.*, 1897, *71*, 250) (1·5 g.) was fused in an oil bath maintained at 170° and a current of dry hydrogen chloride passed over it during the course of an hour. The molten azine solidified to a mixture of the pyrrole and ammonium chloride, the latter appearing as white crystals on the surface. After cooling, the mass was extracted with glacial acetic acid. The pyrrole, which remained undissolved, was filtered-off and recrystallised from pyridine. It was thus obtained as very pale green shining needles (0·5 g.), m.p. above 360°.

Found: N=5·9%; calculated for $C_{18}H_{13}N$, N=5·7%.

ACKNOWLEDGMENTS.

The authors gratefully acknowledge the assistance of a grant from the Commonwealth Government Research Fund, and of a scholarship from the same fund held by one of them (R.H.H.), during the tenure of which the work was carried out.

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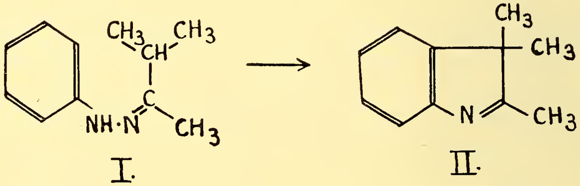
RESEARCHES ON INDOLES.

PART VI.—APPLICATION OF THE FISCHER SYNTHESIS TO SOME CYCLOHEXYL KETONES.

By GORDON K. HUGHES, B.Sc.,
and FRANCIS LIONS, B.Sc., Ph.D.

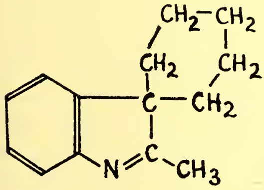
(*Manuscript received, November 17, 1937. Read, December 1, 1937.*)

Plancher (*Berichte*, 1898, *31*, 1496) appears first to have noticed that the Fischer cyclisation of ketone phenylhydrazones to indoles occurs especially easily when one of the alkyl groups attached to the carbonyl group of the ketone is a secondary alkyl group. The product of the reaction then is a tertiary base of the 3 : 3-disubstituted indolenine type. Thus, the phenylhydrazone of methyl isopropyl ketone (I) passes over very readily to 2 : 3 : 3-trimethylindolenine (II), and 2-isopropylindole is not formed at all. Even the methyl phenylhydrazone of methyl isopropyl ketone behaves in a similar way, and here the elimination of ammonia occurs so easily that an indolenine (or the anhydro base therefrom) is formed even by simple contact in the cold of the hydrazone with alcoholic zinc chloride solution (cf. Plancher, *loc. cit.*; Jennisch, *Monatsh.*, 1906, *27*, 1223). Gogin (*Monatsh.*, 1906, *26*, 731) extended the reduction to the phenylhydrazone of isobutyraldehyde, and showed that from this, 3 : 3-dimethylindolenine could be obtained very easily by warming at 60° with alcoholic zinc chloride.



Further examples of indolenine ring closure rather than indole ring closure are to be found in the cyclisations of the phenylhydrazones of 2-substituted cyclohexanones, when 11-substituted tetrahydro-carbazolenines are formed as well as small amounts of 1-alkyl tetrahydrocarbazoles. (Cf. Plancher and Testoni, *Gazzetta chim. Ital.*, 1900, *30*, ii, 558 ; *R.A.L.*, 1900 (v), *9*, i, 218).

It appeared, therefore, that methyl cyclohexyl ketone would form a phenylhydrazone which would undergo the Fischer synthesis with ease to form 1-cyclohexane-3-(2-methylindolenine)-spiran (III) rather than 2-cyclohexylindole (IV) ; and experiment has now shown this to be so. Solution of methylcyclohexyl ketone phenylhydrazone in hot glacial acetic acid followed by a few minutes' heating suffices for the formation in good yield of (III). In a similar way, the phenylhydrazones of phenylcyclohexyl ketone (V), p-anisylcyclohexyl ketone (VI), and veratrylcyclohexyl ketone (VII) can be readily cyclised to the corresponding 1-cyclohexane-3-(2-arylindolenine)-spirans (VIII).



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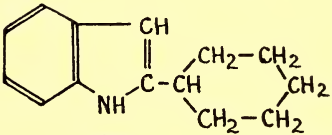

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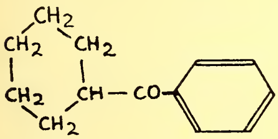

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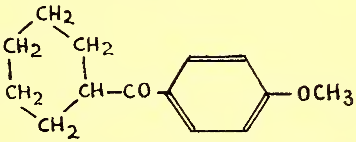

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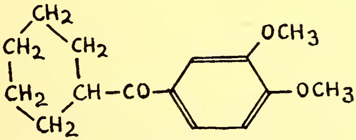

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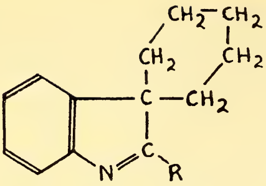
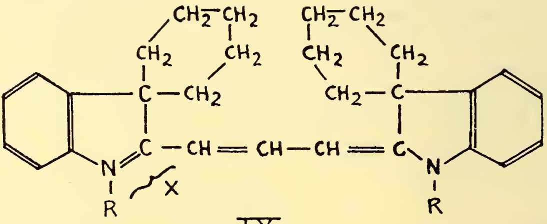


(R = C_6H_5, $C_6H_4(OCH_3)$, $C_6H_3(OCH_3)_2$).

VIII.

All these indolenine bases are typical tertiary bases and readily add on alkyl halides to form quaternary ammonium salts.

As was to be expected the quaternary alkyl salts from (III) behave very similarly to the quaternary alkyl ammonium salts of 2 : 3 : 3-trimethylindolenine. In particular, they show the characteristic reactivity of the 2-methyl group, and can be readily condensed with aldehydes, such as p-dimethylaminobenzaldehyde, to form 2-styryl indolenine derivatives, or compounds of the benzylidene bis (indolenine) type. Also, with ethyl orthoformate in dry pyridine solution they readily form dyestuffs of the carbocyanine type (IX) (cf. Hamer, *J.C.S.*, 1927, 2796).



IX.

We have not studied the effects of heat on the quaternary alkyl ammonium salts of (III), preferring to reserve discussion of the very remarkable shifts of alkyl groups observed with substances of this type until we have had an opportunity of preparing and examining the indolenine from methyl cyclopentyl ketone.

EXPERIMENTAL.

Methyl cyclohexyl ketone.

Methyl cyclohexyl ketone was prepared by the method of Nenitzescu and Cioranescu (*Berichte*, 1936, 1821) in 50% yield (yields of 70% are claimed by N. and C.).

The dinitrophenylhydrazone of (I) was prepared by the method of Brady (*J.C.S.*, 1931, 757) and recrystallised from ethyl alcohol. It came down in brilliant orange plates, m.p. 128°.

Found: N=18·4%: calculated for $C_{14}H_{13}N_4O_4$, N=18·3%.

1-Cyclohexane-3-(2-methylindolenine)-spiran (*III*).

Methyl cyclohexyl ketone (12·6 g.) and redistilled phenylhydrazine (10·8 g.) were mixed. An immediate reaction took place with evolution of heat and elimination of water. To complete reaction the mixture was warmed at 100° for thirty minutes. After cooling and separation of the water formed in the reaction, the remaining oil could not be induced to crystallise. It was dissolved in ether, dried, and the solvent removed. To the residual oil glacial acetic acid (50 c.c.) was added, the colour immediately changing from orange to dark green. The solution was refluxed for thirty minutes, then cooled and basified and the brown oil which separated extracted with ether. To remove any unchanged ketone the ether extract was shaken three times with dilute hydrochloric acid, the acid extracts combined, washed with ether, and basified with caustic soda. The indolenine which separated as an oil was again extracted with ether, dried, and after removal of the solvent distilled *in vacuo*. The fraction (11 g.) boiling at 131–134°/2 mm. was collected. It was a light brown viscous oil.

Found: C=83·8, H=8·8%; calculated for $C_{14}H_{17}N$, C=84·4, H=8·5%.

It was not possible to effect the above ring closure by boiling the phenylhydrazone of methyl cyclohexyl ketone with 10% sulphuric acid, hydrolysis occurring under these conditions.

The *picrate* of this base crystallised from alcohol in fine yellow needles which melted at 188°.

Found: N=12·6%; calculated for $C_{20}H_{20}N_4O_7$, N=13·1%.

1-Cyclohexane-3-(2-methylindolenine) spiran-methiodide.

Solution of (III) (10 g.) in methyl iodide (35 g.; excess) led to almost immediate reaction and separation of fine creamy needles of the quaternary salt. After gentle warming for a few minutes the solid was collected (yield theoretical) and recrystallised from methyl alcohol, when it came out in needles melting at 248°.

Found : N=4·2% ; calculated for $C_{15}H_{20}NI$, N=4·1%.

1-Cyclohexane-3-(2-methylindolenine) spiran-ethiodide.

Treatment of a solution of (III) (2 g.) in ethyl iodide (10 g.) in a closed tube at 100° for one hour led to formation of the ethiodide, which was obtained in almost colourless needles after recrystallisation from methyl alcohol. These melted at 252°.

Found : N=4·1% ; calculated for $C_{16}H_{22}NI$, N=4·0%.

3 : 3′-Di(cyclohexane spiran)-1 : 1′-dimethylindocarbocyanine (IX ; R=CH_3).

Hamer's method (*loc. cit.*) was employed as follows: The methiodide of (III) (2 g.), ethyl ortho-formate (3 g.) and pyridine (10 c.c. ; distilled from barium oxide) were heated together at 100°. Almost immediate reaction was indicated by development of an intense scarlet colour. After two hours the solution was cooled and poured into water. The precipitated dye was collected and recrystallised from methyl alcohol, being thus obtained in olive green aggregates which melt at 265°.

Found : I=22·3% ; calculated for $C_{31}H_{37}N_2I$, I=22·5%.

3 : 3′-Di(cyclohexane spiran)-1 : 1′-diethylindocarbocyanine (IX ; R=C_2H_5) was obtained in an exactly similar way from the ethiodide of (III). It came out from methyl alcohol in olive green aggregates melting at 265°.

Found : I=21·3% ; calculated for $C_{33}H_{41}N_2I$, I=21·6%.

1 - Cyclohexane - 3 - (2 - p - dimethylaminostyrylindolenine) spiran methiodide.

A solution of the methiodide of (III) (1·5 g.) and p-dimethylaminobenzaldehyde (4 g.) in methyl alcohol (15 c.c.) was refluxed for four hours. The intensely purple coloured solution deposited purple needles on cooling. After recrystallisation from methyl alcohol these melted at 241°.

Found : N=5·9, I=25·0% ; calculated for $C_{24}H_{29}N_2I$, N=5·9, I=26·9%.

p-Dimethylaminobenzylidene bis (2-methyl-3-cyclohexane spiran indolenine methiodide.

A solution of the methiodide of (III) (2·4 g.) and p-dimethylaminobenzaldehyde (0·5 g.) in methyl alcohol (10 c.c.) was refluxed for three hours. On cooling bright red prisms crystallised together with a small amount of purple needles. By recrystallisation with the help of decolourising charcoal, the colour of the solution diminished and bright red prisms melting at 248° were obtained.

Found: N=5·4, I=33·8%; calculated for $C_{39}H_{47}N_3I_2$, N=5·2%, I=31·3%.

p-Anisyl cyclohexyl ketone (VI).

Equimolecular parts of anisole (15 g.) and cyclohexane carboxylic acid chloride (14 g.) were dissolved in carbon bisulphide (40 c.c.) and aluminium chloride (14 g.) added in small portions with shaking. After allowing to stand for thirty minutes the mass was decomposed with ice. The oil which separated was taken up and dried in ether, and finally distilled *in vacuo*. A colourless oil (12 g.) boiling at 206–208°/26 mm. was collected. It solidified on standing and was further purified by recrystallisation from petroleum ether (40–60°), coming out in colourless needles, m.p. 66°.

Found: C=77·4, H=8·1%; calculated for $C_{14}H_{18}O_2$, C=77·1, H=8·3%.

The dinitrophenylhydrazone of this ketone crystallised from ethyl alcohol in brilliant orange platelets, m.p. 123°.

Found: N=14·2%; calculated for $C_{20}H_{22}O_5N_4$, N=14·1%.

Phenylhydrazone of p-anisylcyclohexyl ketone.

Equimolecular parts of the ketone (VI) (5 g.) and phenylhydrazine (2·5 g.) were dissolved in a small quantity of methyl alcohol and the solution refluxed for one hour. The phenylhydrazone crystallised out as colourless needles on cooling, and after recrystallisation from methyl alcohol melted at 120°.

Found: N=9·4%; calculated for $C_{20}H_{24}N_2O$, N=9·1%.

1-Cyclohexane-3-(2-p-anisylindolenine) spiran (VIII; R=$C_6H_4OCH_3$).

A solution of the above described phenylhydrazone of (VI) (6 g.) in glacial acetic acid (30 c.c.) was refluxed for six hours. It was then poured on to ice, and basified with sodium hydroxide solution. The liberated oily base was taken up and dried in ether, and after removal of the solvent was distilled *in vacuo*. A fraction (3 g.) boiling at 205–210°/1·2 mm. was collected. It solidified on cooling and was recrystallised from methyl alcohol, being thus obtained in pale yellow hexagonal plates melting at 107°.

Found: C=82·5, H=7·3, N=4·8%; calculated for $C_{20}H_{21}ON$, C=82·5, H=7·2, N=4·8%.

The *picrate* crystallised from ethyl alcohol in brilliant yellow needles, m.p. 211°.

Found: N=10·8%; calculated for $C_{26}H_{24}N_4O_8$, N=10·6%.

Methiodide of (VIII) ($R=C_6H_4OCH_3$).

The indolenine was dissolved in excess methyl iodide and heated at 100° for thirty minutes. The methiodide solidified on cooling. It melted at 156°.

Found: N=3·2%; calculated for $C_{21}H_{24}NOI$, N=3·2%.

1 - Cyclohexane - 3 - (2 - phenylindolenine) spiran (VIII; $R=C_6H_5$).

Phenylcyclohexyl ketone was prepared according to the method of v. Meyer and Scharvin (*Berichte*, 1897, *30*, 1942). Treatment of its alcoholic solution in the hot with one equivalent of phenylhydrazine led to ready formation of the *phenylhydrazone* which was obtained as an oil. It was dissolved in acetic acid, the solution boiled for five hours, then poured into water and the indolenine base recovered exactly as described for the derivative of p-anisylcyclohexyl ketone. The indolenine distilled at 195–200°/1·5 mm., and solidified on cooling. Recrystallised from methyl alcohol it was obtained in faintly yellow prisms melting at 86°.

Found: C=87·5, H=7·4, N=5·6%; calculated for $C_{19}H_{19}N$, C=87·4, H=7·4, N=5·4%.

The *picrate* of this indolenine forms yellow needles melting at 170°.

Found: N=11·4%; calculated for $C_{25}H_{22}O_7N_4$, N=11·2%.

The *methiodide* forms faintly yellow needles, melting at 204°.

Found: N=3·5%; calculated for $C_{20}H_{22}NI$, N=3·5%.

Dinitrophenylhydrazone of Phenylcyclohexyl ketone.

Prepared in the usual way this derivative was recrystallised from glacial acetic acid and obtained in orange plates melting at 192°.

Found: $N=15{\cdot}2\%$; calculated for $C_{17}H_{20}O_4N_4$, $N=15{\cdot}2\%$.

Veratrylcyclohexyl ketone (VII).

This ketone was prepared from veratrole, cyclohexane carboxylic acid chloride and anhydrous aluminium chloride by a similar method to that described for (VI). It distilled at 221–223°/20 mm. and solidified on cooling. Recrystallised from petroleum ether it was obtained in small colourless plates melting at 51°.

Found: $C=72{\cdot}3$, $H=8{\cdot}1\%$; calculated for $C_{15}H_{20}O_3$, $C=72{\cdot}6$, $H=8{\cdot}1\%$.

The *dinitrophenylhydrazone* was prepared in the usual way. It crystallised from alcohol in fine orange needles, m.p. 147°.

Found: $N=13{\cdot}1\%$; calculated for $C_{21}H_{26}O_6N_4$, $N=13{\cdot}1\%$.

The *phenylhydrazone* was prepared in alcoholic solution and after recrystallisation from methyl alcohol it formed colourless needles melting at 190°.

Found: $N=8{\cdot}4\%$; calculated for $C_{21}H_{26}O_2N_2$, $N=8{\cdot}3\%$.

1 - Cyclohexane - 3 - (2 - veratrylindolenine) spiran [VIII; $R=C_6H_3(OCH_3)_2$.]

The phenylhydrazone of (VII) was boiled in glacial acetic acid solution as before, and the product recovered in the usual way. It was not necessary to distil it, as the crude oil solidified. After several recrystallisations from methyl alcohol it was obtained in faintly yellow prisms melting at 152°.

Found: $C=77{\cdot}9$, $H=7{\cdot}4$, $N=4{\cdot}5\%$; calculated for $C_{21}H_{23}O_2N$, $C=78{\cdot}5$, $H=7{\cdot}2$, $N=4{\cdot}4\%$.

The *picrate* formed yellow needles (from alcohol) melting at 217°.

Found: $N=10{\cdot}6\%$; calculated for $C_{27}H_{26}O_9N_4$, $N=10{\cdot}2\%$.

The *methiodide* was obtained from methyl alcohol in almost colourless needles, melting at 207°.

Found: $N=2{\cdot}8\%$; calculated for $C_{22}H_{26}O_2NI$, $N=3{\cdot}0\%$.

ACKNOWLEDGMENTS.

The authors gratefully acknowledge the assistance of Miss E. M. Goulston, B.Sc., and Miss J. Spruson, B.Sc., for some of the (micro) analyses recorded in this paper. They also acknowledge with great pleasure the receipt of a grant from the Commonwealth Government Research Fund, which has materially assisted the completion of the work.

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THE SIMPSON DESERT AND ITS BORDERS.*

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(With Plates IV-XI and one text-figure.)

INTRODUCTORY.

I thank the Council of this Society for the honour they have done me in inviting me to give the Clarke Memorial Lecture for 1938. Before I proceed with my lecture, let us first remember the man in honour and memory of whom the lecture was provided for.

The Rev. W. B. Clarke took a degree at the University of Cambridge, where he included in his studies lectures in geology under Professor Sedgwick and Dr. E. Clarke. He subsequently took Holy Orders, and came out to Sydney in 1839. He was rector of the parish of Willoughby for twenty-six years, from which post he retired in 1870, but retained his position as a clergyman in the diocese of Sydney up till his death in 1878. During his thirty-nine years in the colony he devoted all his spare time to geological research, and, though never a professional geologist, he laid the foundations of the geology of New South Wales, and was the unofficial adviser to the government and to innumerable miners and mining interests. His great desire, in which he eminently succeeded, was to render scientific service to the land of his adoption. Among his principal achievements was the elucidation of the fundamentals of the stratigraphical sequence in New South Wales and of the palæontology, and the production of a geological map. He played a principal part, too, in the discovery and stimulation of the production of gold in New South Wales. He was one of the two first Vice-Presidents of this Society, and possibly the first of the few Australians who have been elected Fellows of the Royal Society.

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* Clarke Memorial Lecture delivered to the Royal Society of New South Wales, March 31, 1938.

I was particularly impressed by a sentence in Mr. Clarke's last anniversary address to this Society, delivered in 1876, and, in remembering this splendid pioneer of science in Australia, I would call your attention again to these few words in his last official message to the Society: "Let us do what we can to serve honestly our day and generation, and then we may be assured that posterity, in its own time, will do us justice".

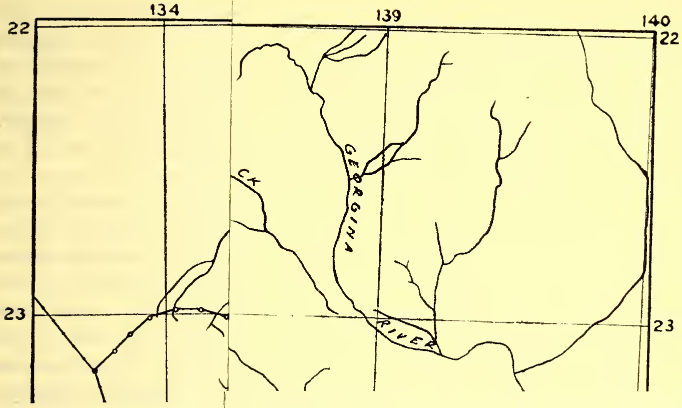
THE SIMPSON DESERT AND ITS BORDERS.

Definition.

The Simpson Desert is a large and distinct physiographical unit, unique in some ways, and possessing many interesting features. Public interest in it has lately been aroused again by Colson's journey across the southern end, and by the loss of Bryce Russell in it and the subsequent aerial search. Little has been specifically written about it, and, as it occupies a portion of three States, no maps show the whole of it in any detail. Thus very little is known about it in civilized places, and, strangely enough, not much more among the people, cattle men, and prospectors, who travel in its vicinity. Some men have claimed to have crossed it when they have merely passed to the north or south of it, and others, ignorant of its nature and even of its position, boast that they would make nothing of crossing it if they had the mind. Actually, no man, white or black, has crossed the middle of it, but several good men known to me have tried and failed. The distances are not excessive as dry stages for camels, but the trouble lies in the never-ending sequence of high sand-ridges, such as few have ever seen, and of the difficulties of which none may speak till they have faced them all the weary day and the succession of days.

My lecture deals with this interesting and desolate region, defining its margins, describing the extraordinary sand-ridges, their origin, shape, and movement, the vegetation and the waters. An outline is given of the geology and physiography of the country on all sides of the desert, and its exploration is summarised from Captain Sturt's expedition in 1845 to my last journey in its vicinity in 1937.

The Simpson Desert was named by me after my aerial investigation of it in 1929, in honour of Mr. A. A. Simpson, C.M.G., who was then President of the Royal Geographical Society of Australasia, South Australian Branch, as it was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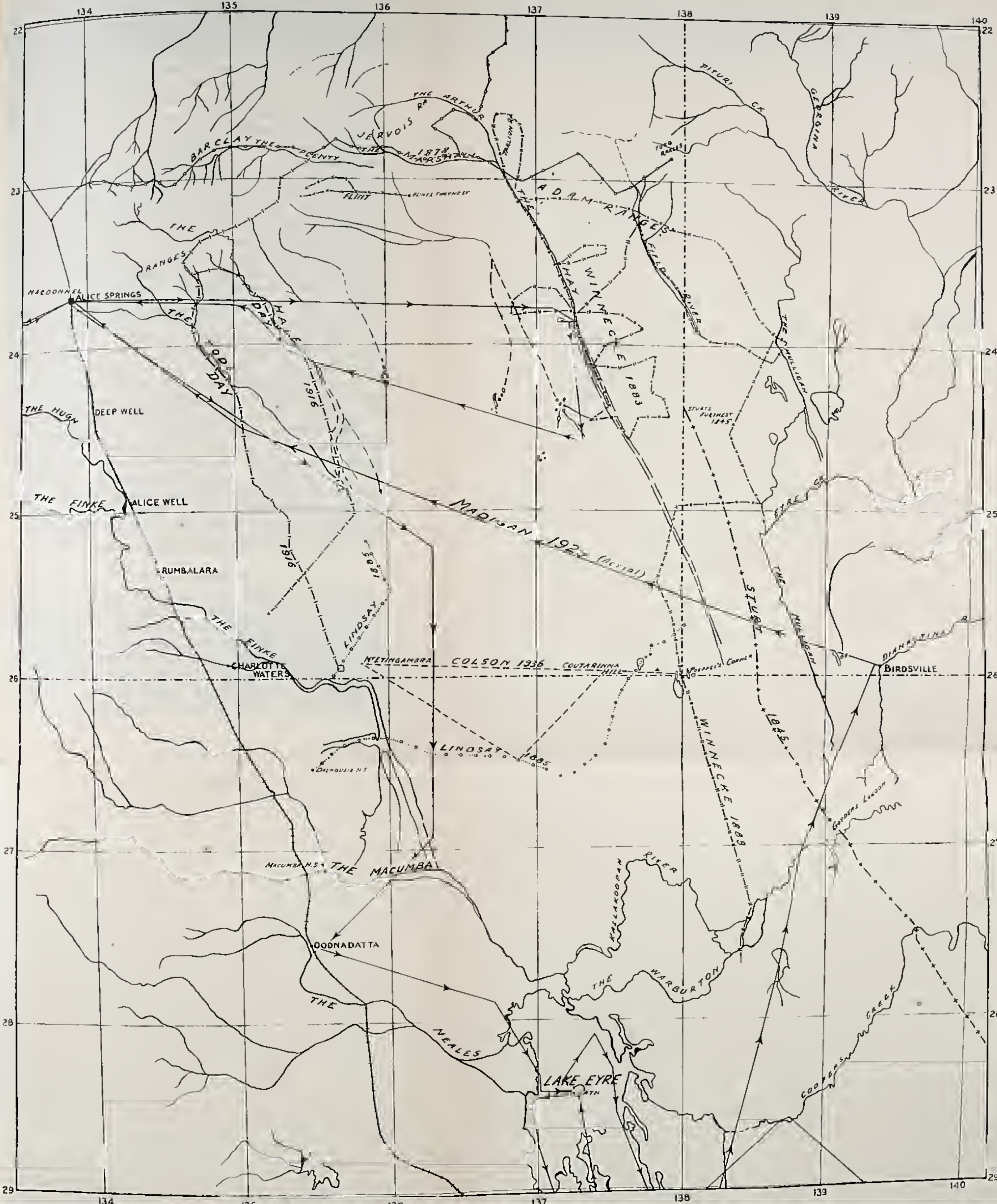
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THE ARTHUR
JERVOIS RA
TARLTON RA
BARCLAY 1878
THE PLENTY
THE MARSHALL
FLINT
FLINTS FURTHEST
TOKO RANGES
PITURI CK
GEORGINA RIVER
THE ADAM RANGES
THE MACDONNEL RANGES
ALICE SPRINGS
THE HALE
THE HAY
THE TODD
DAY
WINNECKE 1883
FIELD RIVER
THE MULLIGAN
STURTS FURTHEST 1845
THE HUGH
DEEP WELL
THE FINKE
ALICE WELL
1916
RUMBALARA
LINDSAY 1885
MADIGAN 1929 (Aerial)
EYRE CK
STURT 1845
THE FINKE
CHARLOTTE WATERS
NTETINGAMBRA
COLSON 1936
COUTARINNA HILL
POEPPEL'S CORNER
DIAMANTINA R
BIRDSVILLE
LINDSAY 1885
DALHOUSIE H.S.
WINNECKE 1883
GOYDERS LAGOON
MACUMBA H.S.
THE MACUMBA
KALLAKOOPAH RIVER
OODNADATTA
THE WARBURTON
THE NEALES
COOPERS CREEK
LAKE EYRE

with Mr. Simpson's help and under the auspices of the Society that I made the investigation. I then applied the name to the "unknown area", inside the routes of previous explorers, but some of these routes lie well inside the desert, which is a distinct unit whose borders are capable of fairly close definition on physiographical lines. The area now to be defined is beyond all permanent occupation and its chief characteristics are level plains covered with sand-ridges and spinifex, absence of surface waters unless under exceptional conditions, and lack of watercourses completely crossing any part of it. Under these limitations its margins are the Mulligan River in the east, the Diamantina and its branch the Kallakoopah in the south down to Lake Eyre, the Finke River as far upstream as the Hugh junction in the west, the MacDonnell Ranges to the north-west, and the Marshall River in the north. The area inside these margins is covered with parallel sand-ridges, and spinifex is almost universal. Several streams from the MacDonnell Ranges flood out into it, but none succeed in crossing it. There is no permanent water in it with the exception of some artesian springs in the south, and no hills or ranges. The sand-ridges extend further east than the Mulligan River, on a diminishing scale, but here there are intermittent streams and grassy flood plains, and to the south-east they cross the flood plains of the Cooper and Diamantina, where, though more scattered, they are of remarkable size and continuity, but this country with its maze of lakes, is again very different from the true sand-ridge desert. The desert lies roughly between latitude 23° and 27° south and longitude 135° and 139° east. Most of it occupies the south-eastern corner of the Northern Territory, but it extends eastward into the south-western corner of Queensland and southward into South Australia, coming to a point at Lake Eyre.

Its area is approximately 56,000 square miles.

Historical Review.

The Simpson Desert was first seen and entered in 1845 by Captain Charles Sturt,(1) the pioneer of the Murray. It was on an attempt to reach the centre of the continent, and is one of the greatest but least known of the journeys of the early explorers. Sturt, then Surveyor-General of South Australia, left the Darling near where Menindie now stands, and went north, discovering and naming the Barrier Ranges, the Strzelecki, Cooper, and Eyre Creeks, and being finally defeated when within 150 miles of his goal by that dreadful waterless sea of sand-ridges and spinifex, the Simpson Desert, by his reckoning in latitude 24° 40′ S. and on the 138th meridian, now the Queensland-Northern Territory boundary.

After crossing the plains south of the Diamantina, and the area at Goyder's Lagoon, free of sand-ridges (Sturt's Stony Desert), Sturt wrote: "It is a remarkable fact that here, on the northern side of the Desert, and after an interval of more than 50 miles, the same sand-ridges should occur, running in parallel lines at the same angle as before, into the very heart of the interior, as if they absolutely were never to terminate". Of his turning point he wrote: "We had penetrated to a point at which water and feed had both failed. Spinifex and a new species of Mesembryanthemum....were the only plants growing in that wilderness, if I except a few withered acacia trees about four feet high. The spinifex was close and matted, and the horses were obliged to lift their feet straight up to avoid its sharp points. From the summit of a sandy undulation close upon our right, we saw that the ridges extended northwards in parallel lines beyond the range of vision, and appeared as if interminable. To the eastward and westward they succeeded each other like the waves of the sea. The sand was of a deep red colour, and a bright narrow line of it marked the top of each ridge, amidst the sickly pink and glaucous-coloured vegetation around." This description might apply to almost any part of the Simpson Desert. It is typical of the whole.

Sturt's decision to turn back was made with a heavy heart. It was a right one, considering the state of the party and of the horses, and the uncertainty of what lay ahead, and in the light of present knowledge it is obvious that to have continued would have meant the destruction of the whole party. He would have been lucky to have found water even in the Tarlton Ranges 150 miles away across the Simpson Desert, an impossible journey without camels, and difficult enough with them.

Sturt's draughtsman on this journey was J. MacDouall Stuart, who subsequently crossed the continent in 1861, passing to the west of the Simpson Desert and completely avoiding it.

The tragedy of Burke and Wills occurred during Stuart's successful journeys, and in 1861-2 McKinlay led a relief expedition from Adelaide. He carried on the reconnaissance of the Cooper in South Australia, and then continued north right to the Gulf of Carpentaria, repeating Burke's journey much more successfully and usefully. This journey was well to the east of the Simpson Desert, and mainly to the east of the Diamantina, which was still not recognised as a continuous stream. McKinlay crossed it at Middleton Creek, and Sturt at Goyder's Lagoon.

In 1876 the Queensland Government sent out an expedition under W. O. Hodgkinson(2) to explore the western side of the State. This expedition discovered and named the Mulligan and ran that stream up N.N.W., finally to leave it and discover the Cairns Range on the 138th meridian, now known as the Toko Range, whence they continued north to the Georgina or Herbert River. This journey was a northern extension of Sturt's, and practically defined the eastern side of the Simpson Desert. After leaving the Mulligan the party was in spinifex and sand-ridges till they reached their Cairns Range.

Both Sturt's and Hodgkinson's longitudes are necessarily unreliable. Hodgkinson on his map shows Sturt's journey well to the west of his Mulligan River, which would mean that Sturt's Eyre Creek was not the Mulligan. The Mulligan divides into several channels near the South Australian border, and it is possible that Sturt followed a channel more to the west. On Queensland maps the southern part of the Georgina, after its junction with the Hamilton, is called Eyre Creek right down into South Australia, including the portion which Hodgkinson first saw and named the Mulligan, near the South Australian border, while the name Mulligan is applied to the north-south watercourse joining Eyre Creek in latitude 25°, that is, the upper part only of Hodgkinson's Mulligan. This gives correct priority to Sturt, but the South Australian and Commonwealth practice is to retain Hodgkinson's Mulligan River intact, and to call the branch joining it from the north-east Eyre Creek, in country not seen by Sturt. This nomenclature is too well established to alter now, so it will be followed in this account. The watercourses in S.W. Queensland, as in so much of the central regions, consist largely of scattered channels and claypans, so that it is almost impossible to define the separate courses. In flood times rivers meet and divide in a crazy pattern in the great flat areas.

After the completion of the Overland Telegraph Line in 1872, the South Australian Government turned its attention to the exploration of the country to the east of the line, with a view particularly to ascertaining its pastoral value, and to consider stock routes.

Eyre was the discoverer of Lake Eyre in 1840. Warburton explored the northern end of the lake in 1866, being second to Sturt in getting a taste of the south end of the Simpson Desert. The surveyor J. W. Lewis⁽³⁾ made a great contribution to the knowledge of the Lake Eyre country by his Lake Eyre Expedition of 1874-5. He practically completed the mapping of the lake and continued his reconnaissance up the Warburton and Diamantina (which he called the Everard) to beyond where Birdsville now stands, thus skirting the south-east end of the Simpson Desert. He also connected the Cooper with Lake Eyre from Innamincka.

For the first time the north end of the desert was visited in 1878 by H. Vere Barclay,⁽⁴⁾ working out from Alice Springs. He followed down the Plenty River and then crossed to the Marshall, and discovered the Jervois Range. Two of his men continued on eastward, passing south of the Tarlton Range without seeing it, and ending up almost at the Queensland border, north of latitude 23° and just south of Hodgkinson's Cairns Range. This journey crossed the northern end of the desert. Another South Australian surveyor, Charles Winnecke, was in the country at the same time, sketching and route surveying the MacDonnell Ranges and the country to the north-east,⁽⁵⁾ between 1877 and 1881. During this period he came down from the Herbert River and discovered the Tarlton Range, and also visited the Marshall and Plenty Rivers. But Winnecke's most hazardous task was his work in 1883,⁽⁶⁾ when he made extensive journeys on the eastern side of the desert, on both sides of the 138th meridian. From Cowarie Station near the Warburton River in South Australia he went northward to Poeppel's Corner, the boundary post where Queensland, South Australia, and the Northern Territory meet, thence up on the west side of the 138th meridian to latitude 25°, then across into Queensland to the Mulligan and up to Sandringham Station. From Sandringham he returned westward and went up the Field River to the hills he named the Adam Ranges, and across to the Hay River, which he discovered and named. He followed up the Hay to the Tarlton Range of his former expedition. He then followed the Hay down, discovering Lake Caroline on the way, to about latitude 24° 33′, where it consisted of six wide flooded flats separated by high sand-ridges. He made considerable diversions into the sand-ridges on both sides of the river. There is no evidence that anyone has visited the Hay below Lake Caroline on the ground either before or since Winnecke was there, and his traverses remain the eastern limits of exploration of the Simpson Desert from the ground. This journey was done entirely with camels. At one period the camels marched 278 miles in sixteen days without water, in what Winnecke described as the heaviest and worst sand-hill country in Australia.

In latitude 25°, in the neighbourhood of the 138th meridian, he wrote: "This country is a perfect desert and I am afraid will never be of much use to the squatter. I am almost certain that this country has never been visited by natives."

From 1875 to 1886 the South Australian Survey Department was very busy in the arid north. The north-east boundary of the State was surveyed, Poeppel completing the east-west line to Poeppel's Corner in 1878. In 1883 the survey of the State boundary from this corner north to the sea, the 138th meridian, was begun, and finished in 1886. The veteran explorer and surveyor Mr. L. A. Wells was assistant surveyor in this work, never leaving it from beginning to end. Carruthers relieved Poeppel as chief surveyor half-way through. The survey of this line gives exact information on the eastern side of the desert. Tracings of it kindly supplied by the Commonwealth Survey Department at Darwin show every sand-ridge.

At this time trigonometrical surveys were also in hand in the far north of South Australia. A survey was run up from the east side of Lake Eyre to tie with Poeppel's Corner, and another up the western side of the southern tongue of the desert to the 26th parallel, its eastern boundary being the Finke. At the border, the 26th parallel, the most easterly Trig. Station was Mt. Etingambra, ten miles west of the 136th meridian, and on the eastern side of the desert, the most westerly point was Coutarinna Hill, twenty-five miles west of Poeppel's Corner, leaving 109 miles across the desert along the boundary still untraversed. This line was travelled by Colson in 1937, as mentioned below. With it as a base an empty triangle of desert stretches south on official maps with its apex on Lake Eyre. Only Lindsay's unofficial journey might be added to this area.

David Lindsay⁽⁷⁾ next whittled away some of the unknown core of the desert in 1885. His intention was to cross it from south to north; in this he failed, but he penetrated it for a considerable distance, and travelled round it on three sides, from Poeppel's Corner to the Tarlton Range, only omitting the east side. The first part of his journey was from Dalhousie Springs eastward and then north-eastward to the Queensland border north of Poeppel's Corner. He discovered a number of artesian springs on the eastern side of his traverse, and was the first to cross the southern end of the desert north of the Macumba and Kallakoopah. He encountered sand-ridges the whole way, with more claypan country to the east. He next tried to penetrate the desert from the Finke east of Charlotte Waters, near where Anacoora Bore now is. He travelled in a N.E. direction, and then N.N.W., with the intention of cutting the Todd River. However, at the end of three days he turned back, considering that the task was too much for the camels, owing to the sand-ridges, and intense heat. His story was the same as Winnecke's, nothing but sand-ridges and spinifex. He returned to the Finke, which he followed up to Alice Well on the Hugh, and thence N.E. to the Giles River and the Hart's Ranges, the Plenty, the Marshall, and Tarlton Range, almost circumscribing the Desert.

T. E. Day,⁽⁸⁾ then Surveyor-General of South Australia, after a long period barren of exploration, succeeded in 1916 where Lindsay had failed. He and his parties from the Finke crossed to the junction of the Todd and Hale and ran the Hale up into the ranges, and followed up most of the course of the Todd.

Then, in 1929, I set out on my aerial reconnaissance of the dry lakes of South Australia and the south-eastern portion of Central Australia.⁽⁹⁾ At that time the Hale was the western, the Hay the eastern, the Marshall the northern, and Lindsay's journey the southern unit of human penetration into the Desert. On this expedition three flights were made across the Desert, one direct from Birdsville to Alice Springs, a second eastward from Alice Springs to Lake Caroline, thence fifty miles southward, and return to Alice Springs, and the third from Alice Springs south-eastward towards the centre of the Desert, then southward to Oodnadatta. These flights showed once and for all that there were no ranges hidden inside the desert margins, but the features were everywhere uniform, sand-ridges and spinifex being universal, and the only variations the changes in the variety and relative sparseness of the larger trees and shrubs, the occurrence here and there of areas of claypans, and the presence or absence of sand between the sand-ridges. The work was done with two Royal Australian Air Force Wapitis, and a large collection of oblique and vertical photographs was made. In addition to the examination of the Desert, the dry lakes were thoroughly investigated, particularly Lake Eyre, to which a ground expedition was made by myself in the same year.(10)

In 1935 I made a motor truck journey from Alice Springs through the Jervois Ranges to the Tarlton Range, thence to Tobermory Station on Piturie Creek and down the Queensland border to the Toko Ranges. In 1937 I returned to the Tarlton Range, which I examined thoroughly. These journeys convinced me that the Marshall River was the natural northern boundary of the Simpson Desert, as there are no sand-ridges to the north of it, but a complete change in geology and vegetation, though levelness and aridity continue far to the north of the Marshall.

In 1936 Mr. E. A. Colson, a pastoralist of Blood's Creek, South Australia, made a very successful journey on camels, accompanied by a black boy, from Mt. Etingambra across to Poeppel's Corner and thence to Birdsville, making a deviation to the south on his return. This journey made a chord to the arc of Lindsay's journey, and was the first traversing of the Northern Territory-South Australia border across the Simpson Desert, a line which has never been surveyed. A more ambitious plan of Mr. Colson's to cross the centre of the Desert in 1937 broke down.

An adventurer named Bryce Russell, who boasted that he could cross the Simpson Desert alone, started out from Oodnadatta with camels in the winter of 1937, in spite of warnings, and has never been heard of since. He wrote to me on the day of his departure from Oodnadatta saying that it would be hopeless to search for him if he did not turn up, but giving no indication of his proposed route. The Air Force carried out an extensive search for him, which could have had very little chance of success in that type of country unless the man were alive and could make smoke signals, but he was either camped on some water or dead before the search set out. It would be an unusual thing if all his camels have perished without trace.

Some of them may yet be found, possibly on one of Lindsay's waters in the south.

This historical review may seem tedious, but the accounts of the journeys mentioned, old though most of them are, contain the latest, and in many cases the only, descriptions of the areas they concern. The country is so inhospitable that occupation has not followed up the journeys of the explorers.

The description of the topography and geology of the area which follows is made up from these journals, and my own observations.

The Sand-Ridges.

As has been said, the chief characteristic of the Simpson Desert is sand-ridges and spinifex. The sand-ridges are straight and parallel, like a grid seen from the air. They are not of the immense heights of the sand-ridges of north-west Africa, which rise to 200 metres, but are a modest 30 to 100 feet high, 40 feet being an average figure. They are narrow and remarkably straight, and run continuously for at least 100 miles in places, extending from horizon to horizon in aerial views. In the Cooper and Diamantina country sand-ridges up to 50 miles long have been mapped by the surveyors. The ridges are mostly about a quarter of a mile apart, but in many places the interval is greater. I have shown elsewhere(11) that the trend of the sand-ridges is strictly parallel to the direction of the prevailing wind, which varies in different parts of the Desert, but the general trend is N.N.W. They are longitudinal and not transverse ridges, with respect to wind direction. They are comparatively symmetrical in cross section, but the N.E. side is universally the steeper. They are fixed by vegetation, mainly spinifex, the only signs of movement being along their length. The N.W. ends can be seen to be extending in small aprons of loose sand, while the S.E. ends show signs of ablation, the spinifex or cane-grass tufts standing up on pillars of sand. This observation has been made in the S.E. part of the Desert, near the Diamantina, and in the environs of Birdsville, where it is most marked. In dry seasons the sand-ridges extend out on to the flood flats in the whole of the Cooper-Diamantina delta, in occupied country where the general movement of the sand is well known to be along the length of the ridges and in a N.N.W. direction. The crests of the ridges are always composed of loose sand in wavy lines, and show the effects of secondary winds (winds other than the prevailing winds). These winds make minor crescentic dunes on top of the ridges that change their form with changing winds. The steep side of the crest may be in the opposite direction to the steep side of the ridge.

There are no barchans in the interior of Australia. There are never any lines of sand running out at an angle to the ridges. Ridges occasionally coalesce in a tuning-fork arrangement, when the stem of the fork is always to the N.N.W. The inter-ridge areas are sometimes swept clear of sand, when they may be gibber plains as in the Diamantina delta and near Birdsville, or they may be long narrow claypans, often connected with river courses, as is usually the case near rivers or where rivers flood out, when they may be well grassed. Sometimes over wide areas the inter-ridge spaces are also covered with sand, as in the central parts of the Desert. Around all the southern borders of the Desert from east to west the sand-ridges are wavy and straggly, though preserving a constant general direction. Towards the interior they straighten out and become almost perfectly straight parallel lines. In the north they die down again, but the straggly appearance is not repeated. They merge into a sandy plain with increasing vegetation to the north. The margin of the definitely sand-ridge country as distinct from sandy plains is marked on the map, Plate I.

The sand-ridges extend from Poeppel's Corner for 180 miles northward. Along this meridian they average thirty to fifty feet high, and there are from four to six of them to the mile measured across their trend. Every ridge is marked in the survey. Their trend is N. 20° W. at the Corner, gradually swinging westward to N. 40° W. at 180 miles, their northern limit. Along the 26th parallel Colson found a series of high parallel sand-ridges, which he described as occurring in groups, about two miles across, with some ten ridges in a group, the groups separated by narrow flats. In each group the ridges were not separated by flats, but the bottom of one led at once to the ascent of the next, the ridges gradually rising to a summit in the centre, so that the whole effect was like one huge serrated sand-ridge two miles across. On his deviation southward he found the ridges more scattered and much more easily negotiated. Nothing like this grouping was seen in any of my aerial flights.

The Alice Springs railway line crosses a spur of the desert north of the Finke, an area known as the Depôt Sandhills. There the ridges are straggly and typical of the margins. The railway runs parallel to them, in a direction N. 17° W.

The general description given at the beginning of this section applies to all the ridges seen on my flights inside the Desert borders. The sand is a fine quartz sand of a striking red colour, very different from the usual yellow of desert sands. Its appearance is similar to that of the sand commonly used in hour glasses. It is white only to the east of the Diamantina, in the delta country of South Australia, becoming redder with distance to the north-west.

The Waters.

There are no absolutely permanent and reliable waters inside the margins of the Simpson Desert as I have defined them, with the exception of Anacoora Bore and the springs discovered by Lindsay in the south. Most of the Desert except in the north is on the artesian basin, and from Lindsay's description, where he mentions water bubbling up, there is little doubt that his springs are mound springs. Similar springs occur on the east side of the Desert in latitude 24°, between the Mulligan and Eyre Creek, where Winnecke mapped six groups.

The drainage is everywhere to the south-east, all the streams rising in the MacDonnells to the north-west or the highlands in the north. The focus of the drainage system is Lake Eyre, which is, in its southern part at least, below sea level. The Finke on the west side of the Desert reaches Lake Eyre in exceptional floods, and the Mulligan and Eyre's Creek on the east may also reach the Diamantina and eventually empty their waters into Lake Eyre, but the streams between them, the Todd, Hale, Illogwa, Hay, and other intermediate unnamed streams all flood out in the Desert. Waterholes may last from one wet season to the next, but when there are no good rains for several years all waterholes go dry. Even after the surface waters are all dried up, water may be got in the sand by digging soaks in suitable localities, but this is always a hazardous business.

After good rains the Todd may be followed down with safety to its junction with the Hale, where they both flood out. Similarly the Hay can be traversed after exceptional rains. Between the Hale and the Hay the only chance of water is in the odd claypans in the north, where surface water would last only a few weeks after rains. The central portion of the Desert between latitudes 25 and 26, where all is sand, would always be waterless.

Winnecke in 1883 relied on a single native well in the Hay, in latitude 23° 48′ 15″, on the east bank of the Hay. He marked a tree near it and said no one travelling the east bank just above Lake Caroline could miss it. He calculated the supply as a thousand gallons a day in a year following rain. This was his sole supply for his journeys up and down the Hay ; the native name is Yarracurracoo. There is now a dogger's camp on the Hay one mile below the junction of the Arthur and Marshall, on the right bank, with a good soakage well and garden. This water is permanent. The man has lived there for over ten years.

Water is almost permanent in the Tarlton Range, in the Algamba Creek, that flows out north past Mt. Guide. There are several waterholes in the creek in the range, the chief one being known as Dutchelbar, four miles south from the northern extremity of the ranges. There was plenty of water there in June of 1935. Another waterhole called Jindinjira lies in the bay in the range in the western side, near Winnecke's Goyder's Pillars and three miles due east of the "pillars" on the Arthur. Aborigines were camped on this in June, 1937. There is a good waterhole, semi-permanent, and a well with small permanent supply, in the Unkah Creek, four miles east of the Jervois Range mine workings, and a permanent timbered soak in the Arthur Creek at the crossing east of the Jervois, known to the natives as Etuckera. There are permanent springs on the north and west sides of the Toko Range, and waterholes in Linda Creek. The spring at the north end of the ranges is called Alcoora, where there are troughs and improvements.

In his Adam Ranges, on the headwaters of the Field River, Winnecke located several waterholes, the principal being Alanajeer in latitude 23° 12′, which he said was not permanent, as the bed of the river is everywhere sandy. Alanajeer is 400 yards long, twenty yards wide, and ten to twenty-five feet deep. He reported finding opal about ten miles north-east of this waterhole, but nothing more has been heard of opal in this region.

The Field River, like the Hay, cannot be relied on for water except after rains, but water is now plentiful for the traveller along the Mulligan. There are many artesian bores along the upper Mulligan from west of Sandringham

Station, in latitude 24°, up to latitude 23°, and numerous perennial springs in that area in addition to those discovered by Winnecke. The most southerly bore is Woolcanare, on the east bank of the Mulligan and one and a half miles east of the main channel, approximately in latitude 29° 45′ S., longitude 138° 40′ E. This bore is seven miles south-east of the angle in the Rabbit Board fence. Seventeen miles down the Mulligan from this bore there is a large waterhole that appears to be permanent, one of Winnecke's camps, in latitude 24° 57′ 35″, near where Eyre Creek joins the Mulligan. The abandoned Kaliduwarry Station is nine miles below the waterhole. Annandale Station is abandoned, but eight miles below it, in latitude 25° 28′, there is Dickerrie waterhole, which I am told on very good authority is absolutely permanent. Alton Downs on the Mulligan, nine miles beyond the South Australian border, is an occupied homestead.

Woolcanare bore, or the waterhole south of it, is the natural goal for anyone making a west-east crossing of the Desert through its centre, starting from the Hale-Todd junction. The definitely permanent waters round the margin of the Desert may be stated as Anacoora and Andado bores on the west side, then the railway line to Alice Well (Bundooma), the eastern MacDonnells at Love's Creek and Arltunga, the Plenty wells, the Marshall Bar, the Marshall-Arthur junction well, the Toko Ranges springs, the Mulligan as described above, and the Birdsville-Maree stock route with Goyder's Lagoon, Mt. Gason, and other bores.

The orientation of everything in the Desert is determined by the trend of the sand-ridges. The streams follow it exactly, and the railway conforms to it where it enters the Desert. The claypans are long and narrow, bordered by sand-ridges.

The streams before they flood out usually form numerous channels and finally end in series of claypans, the continuity of which is hard to establish. I added a few of the major groups of claypans to the map in the north end of the Desert on my aerial reconnaissance, and suggest that they are supplied by the streams to which they are connected by dotted lines. There must be many more claypans in the southern end, as indicated by the mapping done by the survey south of Poeppel's Corner, but in the central parts they are absent. The Hay was traced to the 138th meridian by Winnecke, where it is broken up into claypans.

Its further continuance is problematical, but there is some indication that it runs further in high floods. On one of my flights I crossed a definite watercourse west of the Mulligan which was on the line of the Hay, so I have continued the Hay down across this line. It is possible that Sturt's Eyre Creek was a channel of the Hay.

The Elevation.

The only accurate levelling is that of the railway line to Alice Springs, but aneroid readings are available from different points round the margins of the desert. The bed of Stuart's Creek under the railway, on the south side of Lake Eyre South, is thirty-five feet below sea level. The lowest point on the railway is at mileage 496¾ from Adelaide, seven miles east of Curdimurka Siding (Stuart's Creek), where the rails are twenty-five feet below sea level. At the Finke Siding the level is 884 feet above sea level, and at Rumbalara in the western edge of the Desert, 1,058 feet. Alice Springs is at 1,905 feet. The MacDonnell Ranges area stands generally at 2,000 feet. On the Queensland side, aneroid heights of about 500 feet have been established on the lower Hamilton River in the Boulia area, 360 feet at Abbotsford Station on the Cooper, and 425 feet by levelling at Thargomindah. Thus, though the Desert appears to the eye everywhere to be level, actually there is a gentle slope from about 1,500 feet on the N.W. side to sea level at the south end, in 300 miles.

The level monotony of the sea of sand-ridge waves is broken by higher ground only in a few isolated places. To the east of Rumbalara there is a group of flat-topped hills, perhaps 200 feet high, visible from the railway, which would not be included in the Desert if its extent could be marked with any accuracy on the map, and small areas of low rounded hills or mounds were observed from the air in the north-west of the Desert, as shown on the map.

The Vegetation.

Spinifex is almost universal. The exception is in the south-east part of the Desert. It does not extend below the 26th parallel on the 138th meridian. From Poeppel's Corner to the south and east the so-called spinifex (*Triodia*) is replaced by cane-grass (*Spinifex paradoxus*), which fixes the sand-ridges. Spinifex is not a marked feature anywhere south of the 26th parallel, but north of it, in the eastern half of the desert, the spinifex is very dense, almost covering the ground over large areas. A very barren strip of desert, where even spinifex is scant, stretches north-north-east from Anacoora Bore towards the margin of the Desert, with spinifex again denser to the west and in the vicinity of the Hale and Todd junction.

Of the larger timber, eucalypts line all the watercourses, with box gum (*Eucalyptus microtheca*) predominating on the eastern side, and being typical of the Mulligan and Diamantina country. Much finer trees of the white and red gum type are seen in the north-western watercourses, as the Hale, Marshall, and Hay.

Acacias are universal, but different genera predominate in different parts. Mulga (*Acacia aneura*) prefers clay flats and is not common in the Desert; Colson saw some along the 26th parallel. Its chief habitat is in the north-west, in the vicinity of the MacDonnells, where it is the dominant tree. The gidgee (*Acacia Cambagei*) is typical of the eastern side of the Desert. It is found right up the 138th meridian, beginning 16 miles south of Poeppel's Corner. It does not occur on sand-ridges, but occupies most of the flats. It becomes more general as one goes north, and forms forests north of the 23rd parallel and west of the Georgina, outside the sand-ridge country. The needle bush (*Hakea leucoptera*) is very common in the south-eastern part of the Desert. It is almost the only tree in the sandhills near Lake Eyre. The cork bark (*Hakea lorea*) is never plentiful but is found in the flats generally in the known parts of the Desert.

The western part of the Desert shows a different association, which is a very important one in other areas west of the railway line in sandy country, that is, the desert oak (*Casuarina decaisneana*)—spinifex association. This is well seen from the train while crossing the Depôt Sandhills. The desert oak is the best tree the Desert supports. It grows on the sand-ridges as well as on the flats. It is much less frequent towards the east.

At the north end of the Desert the dominant tree is a small and straggly variety of mallee. This is very plentiful in the sandy country on the margin of the Desert south of the Marshall. In the central parts of the Desert, away from the watercourses, trees and shrubs are practically absent, and only the hollow rings of spinifex are seen from the air.

An interesting desert plant is the native tobacco, piturie (*Nicotiana* sp.). The early explorers showed great interest in it, as all native guides knew of the locality where piturie grows ; it has been traded by the natives far and wide in the past. Its principal habitat is in the north-east of the Desert, south of the Toko Ranges. Winnecke reported the piturie bush in great profusion near the Field River in latitude 24°. This particular type of tobacco bush seems to be practically confined to this area, and is still sought by the aborigines of the central regions.

These are merely notes on the vegetation, with no pretence to a complete description, but observations of the more outstanding features. After rains there is a wealth of annuals and ephemerals in the Desert, the most important of which is the parakeelya (*Calandrinia balonnensis*), on which stock can live for months without water. This succulent sandhill plant is universal in the Desert, and after rains it draws the cattle far into the Desert from the bordering stations.

During my 1937 journey, Mr. R. L. Crocker made more complete botanical observations at the Tarlton Range, on the northern fringe of the Desert. Round this range there are splendid grasses, including Mitchell grass. Mr. Crocker determined on the stony tableland of the Tarlton Range the following bushes : *Grevillea Wickhamii*, *Cassia desolata*, *Eremophila longifolia*, *Eremophila Latrobei* and *Acacia Cambagei* (gidgee). Gidgee and bloodwood gum (*Eucalyptus pyrophora*) dominate the flats near the Arthur Creek, while Mitchell grass (*Astrebla pectinata*) and mulga grass (*Aristida arenaria*) are abundant. Along the watercourses coming out of the ranges *Eucalyptus microtheca* (desert box or coolibah), *Atalaya* sp. (white wood), *Ventilago viminalis* (supplejack) and *Santalum lanceolatum* are the most prominent trees, with the under shrubs *Cassia desolata*, *Eremophila Latrobei*, and annuals *Trichinium obovatum*, *Convolvulus erubescens*, *Melothria maderaspatana*, *Cucumis melo* and *Senecio Gregorii*. The grasses of the Tarlton area include *Chloris divaricata*, *Dichanthium humilius*, *Eragrostis xerophila*, *Pollinia fulva*, *Triraphis mollis*, *Panicum decompositum*, *Astrebla pectinata*, *Aristida arenaria*, *Dicanthium sericium*, and *Bothriochloa inundata*.

Climate.

The rainfall of the Simpson Desert is an uncertain quantity, but it averages from five to seven inches annually, so that the absence of surface waters can be readily understood. The good seasons of the country come about once every ten years, when the rivers come down in flood and all the waterholes and claypans are filled. The present rainy season, January and February of 1938, has brought the greatest floods since the white man came into the country, up to six inches falling in a few days. The Desert would at present be easy to cross. The average annual temperature is a little over 70°, according to Weather Bureau statistics.

The dominant wind is the south-east trade, which is never very strong, rarely exceeding twenty miles an hour. The infrequent westerly winds are often stronger, to which the steep easterly slope of the sand-ridges is due. The gentle south-east trades are almost continuous except in the summer months. Clear skies, high temperatures, south-east breezes, and aridity are the characteristics of the weather of the Simpson Desert.

Aborigines.

There is abundant proof that aborigines have never crossed the Simpson Desert between the Hale and the Hay. They have been questioned by interested persons all round the Desert, among whom I have made frequent enquiries. Many prospectors have sought guides among the aborigines, but always with the same result, that they say there is no water, and they fear the Desert as the home of evil spirits. They know the Hale on the west, and Lindsay's Springs in the south. Lindsay was himself guided on his route by an aboriginal. They also know the pituri country to the north-east, and the upper part of the Hay, but the centre is to them *terra incognita*, a sure proof that it is waterless. The Mulligan and Diamantina country was well inhabited by aborigines in the early days, as recorded by Sturt and McKinlay. Many different tribes surrounded the Simpson Desert, the Aranda people of the MacDonnell Ranges being interested only in the north-west corner in the neighbourhood of the ranges.

I have put forward before(12) some argument that the last resting place of Dr. Ludwig Leichhardt's party was the Simpson Desert. There seems no other place where the party could have *disappeared*, so that no remains have ever been found or stories heard by black men or white. The Desert lies across Leichhardt's intended route.

Geology and Physiography of the Borders.

The Simpson Desert itself is covered with recent sand-ridges and clay flats. The margin of the great artesian basin almost coincides with the northern margin of the Desert, so that most of the sand-ridges lie on the basin, which extends below Lake Eyre to Marree and westward to the 134th meridian in the far north of South Australia. The edge of the basin crosses the railway line near Rumbalara in the Desert north of the Finke, where the railways have a bore. Beyond this it has not been traced in the Northern Territory. It has been carefully mapped in Queensland, where the margin comes from west of Boulia across the Georgina south of Glenormiston Station and thence to the Northern Territory border at about latitude 23° 30′. Between Rumbalara and this point nothing of the contours of the basin is definitely known, but on physiographical lines it is safe to assume that its margin would follow more or less the edge of the level desert. The points have been joined on the map, Plate I, by a smooth curve.

The borders of the Desert where it lies on the artesian basin are everywhere somewhat similar and markedly different from the non-artesian rim. On the eastern side, down the Mulligan and Diamantina to Lake Eyre, the country is very flat and featureless, with many dry water-courses and salt lakes and dry claypans. The sand-ridges extend beyond the Mulligan almost to Bedourie, and to about the 140th meridian, east of Birdsville, and occupy most of the north-east corner of South Australia right down to the horseshoe of lakes Eyre, Gregory, Blanche, Callabonna, but in the delta country they are much more scattered and less formidable than in the Desert proper. On this side rock outcrops are few on the plains. The areas free of sand and other than lake beds are usually stony gibber plain, as Sturt's Stony Desert. These gibbers are the results of the weathering of the siliceous crusts of what is known as the Eyrean Series, sandstones, sometimes calcareous, and gypseous shales, of Tertiary age, unfossiliferous except for plant remains in places. This series overlies the Cretaceous beds of the basin, and the present cycle of erosion and deflation has almost removed them. The remnants of the Eyrean beds form scattered flat-topped mesas and buttes throughout the basin country, low table tops 50 to 100 feet high breaking the monotony of the sandy or stony plains. They are conspicuous round

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SIMPSON
DESERT
THE DULCIE RA.
THE ARTHUR
JERVOIS RA.
THE PLENTY
THE MARSHALL
THE HAY
ADAM RANGE
HARTS RA.
THE RANGES
ALICE SPRINGS
BURTS WELL
ARLTUNGA
THE TODD
THE HALE
MACDONNELL
JAMES RANGES
THE HUGH
DEEP WELL
ALICE WELL
THE FINKE
RUMBALARA
M^T PEBBLES
CHARLOTTE WATERS
ANACOORA BORE
M^T ETINGAMBRA
NORTHERN TERRITORY
SOUTH AUSTRALIA
COUTARINNA HILL
POEPPEL'S CORNER
QUEENSLAND
NORTHERN TERRITORY
QUEENSLAND
TOBERMORY STN
PITURI CK
GEORGINA RIVER
GLENORMISTON
FIELD RIVER
M^T EWING
L. CAROLINE
RABBIT FENCE
THE MULLIGAN
BEDOURIE
EYRE CK
L. MACKAY
DIAMANTINA R.
BIRDSVILLE
HAMILTON R.
Margin of Sandridges
Great Artesian Basin
Margin of Sandridges
Margin of Sandridges
MACUMBA H.S.
THE MACUMBA
OODNADATTA
ALGEBUCKINA
THE NEALES
LAKE EYRE NORTH
THE WARBURTON
KALLAKOOPAH RIVER
BOORTHANNA
Goyder's Lagoon
COOPER
Scale - Miles
10 5 0 10 20 30 40 50 60 70 80 90 100

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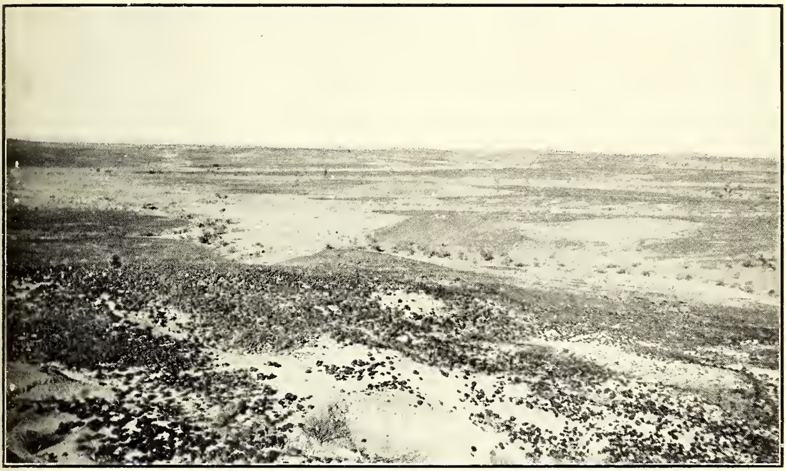

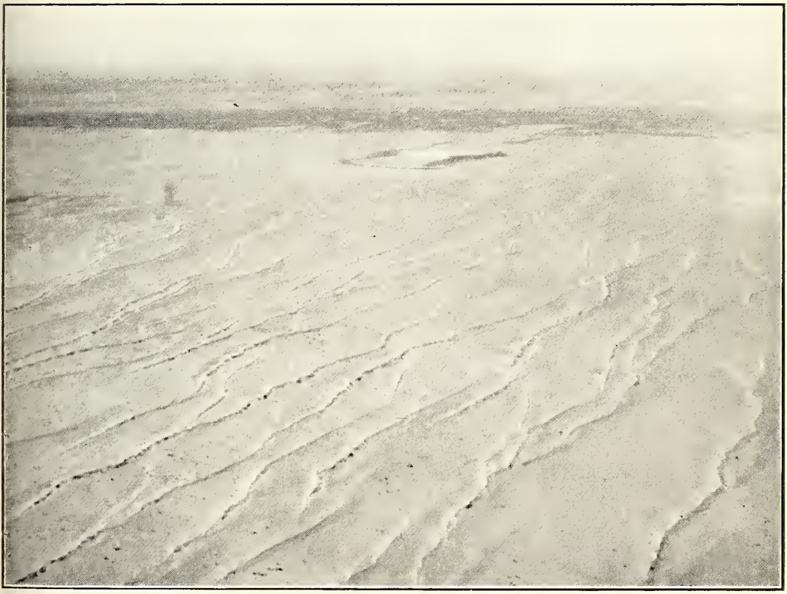

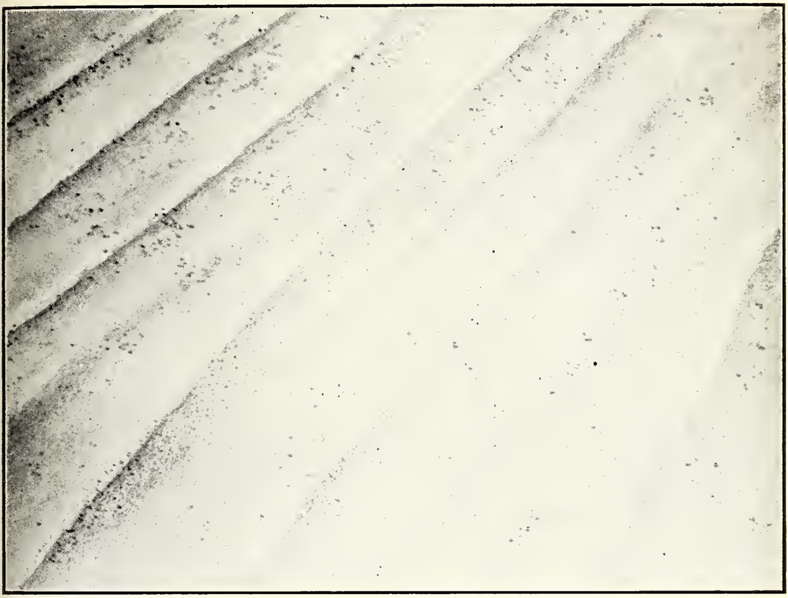

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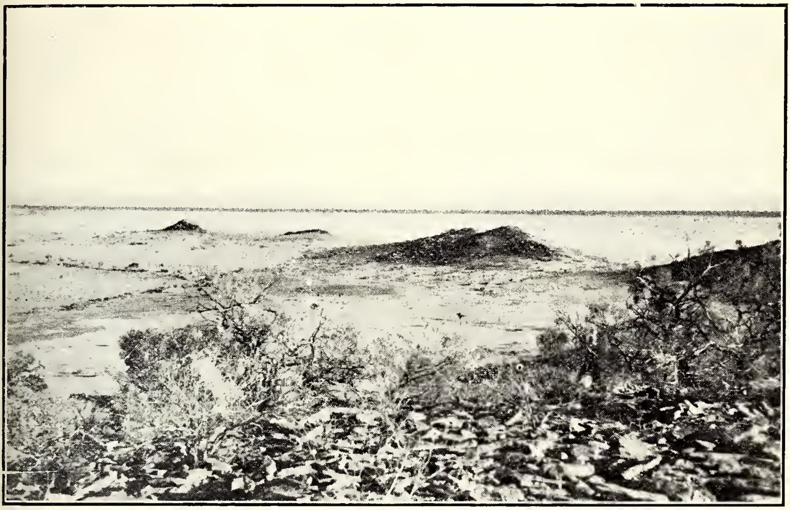
Journal Royal Society of N.S.W., Vol. LXXI, 1937, Plate XI.



Birdsville, where the rock is a yellow calcareous sandstone, the porcelainised capping being dark red. This type of country continues south to the Flinders Ranges, which are composed of Pre-Cambrian sediments, where the rugged scenery is in marked contrast to the barren wastes of the plains to the north.

Round Lake Eyre the flat tops are of gypseous clay, containing beds of selenite several inches thick; large plates of this selenite are a feature of the Lake Eyre country. The surface porcelainisation of the underlying Cretaceous beds in this western part of the Great Artesian Basin makes it difficult to distinguish small mesas of unfossiliferous Upper Cretaceous shales from the Eyrean mesas.

The Mulligan River makes a very definite eastern border to the Desert. The red sand-ridges come right out to it and all the land to the west of the river is unoccupied. A Rabbit Board fence (as it is called) runs up the west side of the Mulligan from the South Australian border to the neighbourhood of Woolcanare Bore, whence it cuts across north-west to the Northern Territory border. The fence is no longer maintained, but we may say that the desert is fenced on this side. The old cattle stations on the Mulligan are at present all closed down. They have been merged into one lease, Glengyle, with headquarters at Glengyle Station on Eyre Creek. Kaliduwarry, Dubbo Downs, and Adria Downs are mere ruins. There is an unoccupied house at Annandale, and a stockman is sometimes at Sandringham. The Mulligan ran in 1921 and in 1933, and it is expected that it may run again this year, 1938; there have been no cattle on the Mulligan since 1933. This dismal story will give some idea of the eastern side of the Desert.

The Field River where it crosses the 138th meridian was called the Gnallanagea Creek by the survey party. This is obviously the same name as Winnecke used for the waterhole on that river higher up in the Territory, namely Allanajeer. This river floods out and can be followed for a short way only in Queensland, not right down to the Mulligan as indicated by Winnecke, according to a station inspector of great experience in the country.

The southern margin of the Desert is the Kallakoopah, a tributary of the Diamantina. The country to the south was once occupied, but all the stations have now been abandoned right down to the Flinders Ranges. This stretch is stony plains with frequent long sandhills trending almost north and south, and few mesas.

The origin of the sand of the Desert is mainly in the disintegration of the porcelainised capping of the Eyrean beds or of the underlying Upper Cretaceous sandstones. The gibbers obviously arise from this cause, and their further breaking down results in sand. The sand is clearly seen to be moving north-west from the Cooper-Diamantina country. One has seen the northern ends of sand-ridges encroaching on trees and watercourses. On Pandi Pandi Station on the Diamantina, a sand-ridge has advanced from the south and crept in between the living rooms and the cookhouse! As it forms the sand is swept into longitudinal ridges which creep north-west. This is still going on in the delta country, but conditions have become fixed further inside the Desert. There are no longer any exposed gibbers or mesas there as a source for more sand; all is covered by sand or clay. The rivers themselves must provide some material from their sediments, which are spread over wide flats and lakes. Most of this sediment would be finer, and be finally removed as dust, but no doubt much sand is carried down in high floods, eventually to become incorporated in the sand-ridges of the Desert under the influence of the trade winds. There is as much sand and desolation between the Kallakoopah and the Flinders Ranges as to the north of the Kallakoopah, where there are also many claypans, but the river courses and occasional floodings bring more good seasons to the south and make the Diamantina a suitable southern boundary to the Desert. The Cooper has not run in its lower courses since 1917.

The south-western border of the Desert in South Australia is clearly defined by the flood plains of the Finke and the Macumba. The Finke waters may in exceptional years reach the Macumba, but the Macumba and Neales are the two rivers which do quite frequently carry their floods into Lake Eyre, where they spread out and evaporate in a few weeks. I have previously shown(10) that Lake Eyre is nowadays never covered with water.

This south-western border is marked by an almost continuous low tableland edge of Eyrean beds, which is dissected by innumerable watercourses, making a fascinating pattern from the air. Flat-topped hills, gibber plains, and wide and wandering watercourses make up the scenery of this Oodnadatta country. Mound springs are frequent right round from Dalhousie to Marree. The flat-topped hills are much larger and more frequent than in the Cooper-Diamantina country. The newest cycle of peneplanation has not gone so far on this side.

Round the southern side of Lake Eyre south there are some outcrops of Lower Cretaceous limestones, occurring as low black-looking mounds near the lake margins ; these are often richly fossiliferous. The railway line from near Bopeechie to Algebuckina follows round the eastern edge of Lower Cretaceous formations, which extend fifty miles and more westward. From Algebuckina through Oodnadatta to the Territory border the Eyrean tabletops dominate the topography. Between Marree and Bopeechie the country is low-lying, but a north-westerly extension of the Pre-Cambrian formations of the Flinders Ranges (in part the Willouran Ranges) runs along the south side of the railway between those points, ending in a group of bold hills at Bopeechie. Two other islands of ancient rock protruding through the Cretaceous, the Mt. Margaret and the Mt. Denison Ranges, making very conspicuous features in the plains, extend along east of the railway between Boorthanna and Algebuckina. These ranges are of lower Pre-Cambrian formations, and show mineralisation in several places, particularly of copper.

The country on the west side of the Desert in South Australia is all occupied, though sparsely. Macumba, Dalhousie, and Blood's Creek are well known cattle stations. Their eastern borders are the Desert.

Near the Northern Territory border the country is very barren gibber plains with few flat-topped hills. The Jura-Cretaceous formations of the artesian basin extend into the Territory and end near Mt. Daniel. At about the Finke Siding a new formation is entered, the Finke River Sandstones. There is abundant evidence of glaciation in these beds, Yellow Cliff on the Finke being a classical locality. The beds are assigned to the Carboniferous period. These sandstones and associated shales extend up the Finke to Idracowra Station and up the Hugh to about midway between Alice Well and Frances Well. This area is distinguished by a marked recurrence of flat-topped hills of sandstone, not distinguishable at a glance from the flat-tops of Eyrean or Cretaceous formations. Crown Point on the Finke, a conical butte with a very small siliceous cap remaining, is a well known example, as is Chamber's Pillar. A stony cape extends north-east from Charlotte Waters into the sand-ridges of the Desert, in which are the two Andado Bores and Mt. Peebles. The author does not know the nature of the formation there; they are probably of the Finke Series. To the east of Rumbalara there is an important group of mesas, in which a commercially important deposit of yellow ochre occurs. These hills as seen from the air strongly suggest Finke Series; they are horizontally bedded. Artesian water is obtained from the Finke sandstones as well as from the Jurassic sands which they underlie. The sand-ridges come right into the Finke in this area.

At Mt. Charlotte, south of Alice Well, a marked change in geology and topography takes place. Here the easterly extensions of the Chandler Range are entered, and from there on to the MacDonnells a series of sandstones and algal limestones is crossed, thrown into gentle folds with an east-west axis. The sandstones are Ordovician and the underlying limestones Cambrian. The limestones extend from Frances Well to Deep Well in the eastern end of the James Ranges. The ridges at Deep Well are the most conspicuous topographical features round the Desert margin since leaving the Mt. Denison Ranges in South Australia, with only the mesas east of Rumbalara otherwise worthy of mention. These sandstone ridges extend eastward from Deep Well across to the Todd River, where they take on a north-east trend, and they form the north-western boundary of the Desert. Although only two miles across at Deep Well, where the railway crosses them, the ridges open out eastwards. For forty miles along the west side of the Todd there are scattered ridges interspersed with flat sandy scrub lands, with four major ridges. These ridges have been examined from the air, but little information was obtained. The capping of these ridges along the Todd is of quartzite, and the dip of all of them is gently to the N.W. Below the capping white soft rock was visible, limestone or weathered shales. They are probably of Ordovician and Cambrian age, rather than of the lower series in the MacDonnells.

A sandy mulga plain separates the James Range from the Ooraminna Range along the railway line. The Ooraminna Range is a counterpart of the Waterhouse Range to the west, and shows Ordovician sandstones overlying Cambrian algal limestones. At Ooraminna Range there is a lack of the general uniformity of strike typical of the formations of the southern MacDonnells, some ridges running north and south near the railway with a suggestion of pitching folds as in the Waterhouse Range. These hills also extend eastward to the Todd River, where the beds are practically horizontal.

The north-west boundary of the Desert is the outliers of the MacDonnell Ranges. The sand-ridges actually lap up against the first range on the Todd River, but eastward of the river there are wide gently-sloping plains from the ranges to the sand-ridges. The height and regularity of the sand-ridges fade out gradually into sandy plains along the northern borders of the Desert, making it impossible to define an exact northern limit of the sand-ridges.

The Ordovician, Cambrian, Proterozoic, and Archæan formations of the eastern MacDonnells and Hart's Ranges send out easterly trending ridges which sink down into these plains, and the numerous streams issuing from the ranges trend away south-east between the sand-ridges far into the Desert, where they eventually flood out. The geology of the eastern MacDonnells has been described by me in a former paper.(13)

The Marshall River, where it joins the Arthur to form the Hay, bounds the northern peak of the Simpson Desert, although the defined sand-ridges end some distance south of the Marshall. They are well developed in latitude 24° and fade out between there and the Marshall. I have recently made two excursions to this area. On the last I rode about ten miles south from the Marshall-Arthur junction and found that sand comes right up to the Marshall, but in ten miles there were no sand-ridges but only very broad and scarcely perceptible undulations. The country was very desert, with abundant spinifex, low straggly mallee, and a grevillea which was mostly dead. From the Marshall-Arthur junction the edge of the sand plains follows the right bank of the Hay south-eastward for some thirty miles to the region of Mt. Winnecke, and then crosses the Hay and trends off more easterly, skirting Winnecke's Adam Ranges, to the Queensland border, where the Field River crosses it, the Gnallanagea of the boundary survey, which is the northern limit of sand-ridges along the border. From the border the sand-ridge and desert margin makes a loop to the north, skirting the hilly area, and then trends away south-east across the Mulligan, passing west of Bedourie and east of Birdsville.

This northern boundary of the Desert, though not defined by the ending of the sand-ridges, is yet clearly marked off. North of it the geology, vegetation, and topography very noticeably change. It is to be noted that all the people living round the Desert or whose lawful or unlawful occasions bring them to its vicinity, regard its margins as those I have laid down. Stockmen, prospectors, doggers, all travel its borders, but they all recognise a line beyond which no one goes, "the Desert". Beyond the northern boundary there are no longer limitless plains to the horizon unbroken by any elevations, but tablelands, small ranges, or isolated hills are always visible. Between the Marshall and the Arthur the land is level, with some sand and spinifex, but it is open forest, with ghost gums (*Eucalyptus papuana*), mulga, grevilleas and hakeas, and the plains are broken by several quartzite ridges or ranges, such as Mt. Cornish, and many low granite outcrops. To the west lie the Jervois Ranges and the Dulcie Range tableland. On the east side of the Arthur at its junction with the Marshall, is the Tarlton Range, a long narrow tableland 300 feet high, with outliers and hills extending south-eastward to Mt. Tietkens and Adam Range, which hilly country causes the indentation in the Desert there. In the area between the Tarlton Range and the Queensland border from Tobermory southward over the Toko Range to the Desert edge, the country is dotted with small and large tablelands and mesas, of which the Toko and Tarlton Ranges are two large ones. One is never out of sight of hills, though their heights are only from 50 to 200 feet. This country has very poorly defined watercourses, though it is stated that the drainage in time of floods is continuous from the Tarlton Range to branches of Piturie Creek. The country is open forest of the type described between the Marshall and Arthur, with spinifex, and grasses in good seasons, and some good bluebush flats, but a noticeable feature from the Arthur eastward is the great increase of gidgee, which is the dominant tree. At the border it makes quite dense woods in places. Mulga decreases with the increase of gidgee.

No sand sufficient to trouble the motorist is met with from Alice Springs to the Jervois Range and eastward to the Tarlton and Queensland border. A motor truck can go anywhere north of the sand-ridge margin marked on the map. From a stocking point of view this country is waterless except after rains. I have mentioned above the permanent waters useful for travellers. The most easterly occupied country on the west side is Huckitta Station, whose cattle do not range beyond the springs round the Dulcie Range, the headwaters of the Arthur Creek. Tobermory is the only station inside the Territory border on the east side in these latitudes, and the wells on Piturie Creek, and the Toko Ranges springs are their only permanent water. However, the country between is not sand-ridge desert. Cattle are taken out into it while surface waters last.

I have made amendments to the maps in the Tarlton Range area. It is rather curious that in regard to this range official maps have followed Winnecke's first sketch map made in 1882, when he sighted and named the Tarlton, and not his map of 1884, when he visited the range. Thus the Arthur Creek is shown cutting across the middle of the range, whereas the range lies entirely on the eastern side of the creek. Goyder's Pillars, too, have not been correctly interpreted. Winnecke first saw them from afar and named them in 1882. When he visited the locality in 1884 he wrote in his journal: " We passed to the westward of two very peculiar white hills, peaks, or pillars, which are situated at the top of a spur in the range. These hills viewed from a distance have the appearance of white pillars; they are crowned by perpendicular kaolin rocks." He marks one hill on his map, on the range at about its centre, and five miles from the Arthur, which he designates " Goyder's Pillars ". He also mentions two long narrow ridges " capped with granite ", clear of the range and on the creek. His route lay between these ridges and his Goyder's Pillars. The two ridges have come to be called Goyder's Pillars quite wrongly. They do not suggest pillars in any way but are narrow quartzite ridges each about a mile long, with the Arthur running between them. The Pillars are actually a disappointment, and obviously on closer inspection not what Winnecke thought they were originally. Lindsay when he passed along the western side of the Tarlton Range was surprised that he could not find Goyder's Pillars, and I spent some time myself on the spot investigating the question. The facts are that the so-called pillars are merely washouts in the side of a mesa on the top of the range, exposing the white sandstone which is full of kaolin. This causes a white triangular streak on the side of the mesa, which is otherwise surrounded by a scree of the dark red debris from the top. There is only one prominent " pillar ", which is visible for ten miles or more on the west side; from a distance it looks like a pillar. There are several other minor "pillars" on this and other mesas on the range, all close together. Local aborigines and a dogger who had been for ten years at the range declared that there was only one white place, this white cut on the side of the hill, which they call Alitcha. Winnecke marks one hill, and this is Alitcha. The aborigines call the two ridges Keepera Keepera, so that I have named them Keepera Ridges, and retain Winnecke's name Goyder's Pillars for Alitcha. The white cut is a distinctive landmark, but not a pillar.

I established latitudes and longitudes (by wireless time signals) at the Tarlton Ranges. Mt. Guide is a conspicuous butte at the north end of the Tarlton Ranges, the largest and most northerly of several outliers. A small and symmetrical butte nearer in may be called Little Mt. Guide. On this a cairn has been built by natives, which I enlarged. This habit of the natives of building cairns, imitating the surveyors, is to be borne in mind when searching for trigonometrical stations. There is a beautifully made cairn about twelve feet high on the flat near Goyder's Pillars, the work of natives.

I have not followed the Marshall River eastward of Mt. Sainthill, but the doggers in the country who know the area so well call the river joining the Arthur the Thring, and maintain that it is the Thring, coming out of the Jervois Range, that makes the main channel running eastward to the Hay. The waters of the Marshall joined by the Plenty apparently flow southward into the Desert. The Marshall Bar, where ridges of rock cross the course of the stream, is regarded as a permanent water by doggers and aboriginals.

I have published a preliminary account of the geology of the northern borders of the Simpson Desert,(14) and will outline it here. The Hart's Ranges, of crystalline rocks, gneisses, schists, granites, and frequent pegmatite dykes, make a bold front to the Plenty plain to the north of them. This plain shows numerous low outcrops of gneiss, with east-west trend. The hills to the westward of the north side of the Plenty plain are also gneissic, with some granite, particularly near Delny Station, but to the eastward there is the broad tableland of the Dulcie Range, of Ordovician sandstone, in front of which is a belt of rugged Cambrian limestone, followed by several quartzite ridges of Pre-Cambrian age, the Mopunga Ranges. A large granite intrusion cuts off the eastern end of the Mopunga Range and separates it from Mt. Sainthill and the Jervois Range. The Jervois Range consists of sandstone ridges in the southern part, trending E.W., and again in the north-eastern part, where the trend is N.N.E. These two lines of ridges enclose a highly metamorphosed area, including many quartz reefs. The sandstones overlie dense limestones, and appear to be older and are certainly more disturbed than the fossiliferous Ordovician tablelands, so that at present I regard them as Cambrian. The gneissic rocks, with granite intrusions, extend eastward from the Jervois Ranges to the Arthur. The Arthur flows round and bounds the gneissic area to the north and east, while the Marshall bounds it in the south as far as outcrops are concerned, for everything is covered with sand south of the Marshall. East of the Arthur and across to the Queensland border all the mesas, including the Tarlton and the Toko Ranges, are of flat-bedded Ordovician sandstones, which rest on limestones. In this whole area outcrops of dense limestone are found at intervals in the low ground, and also to the north of the Dulcie Range and Arthur Creek. This limestone contains some obscure fossil markings, but no Ordovician fossils have been found in it except at the Tarlton Range. It seems most probable that the Cambrian Georgina limestone extends southward and westward right across to the Arthur Creek underlying the whole of the great plains north of the Simpson Desert.

The tongue of gneissic and granitic rock from the Jervois Range extends eastward between the south end of the Tarlton Range and the Desert, in a narrow band at that point. Gneisses with quartz veins occur at the south end of the Tarlton. Of the country south-eastward of that point there are no records except those of Winnecke, but there are persistent rumours of gold having been found in the area, and this is quite possible. There is an area awaiting the prospector between the line Tarlton Range South-Queensland border south of the Toko Ranges, and the sand-ridge desert. North of this line and north of the Arthur, as well as in the Desert itself, prospecting would be quite futile. This country could be worked only in good rain seasons, but it would then present no great difficulties. Only time prevented me from continuing across it in my truck on my last expedition. Winnecke said that his Mt. Tietkens was composed of red granite, Mt. Smith was granite capped by ironstone, and " hornblende, mica, quartz, and other rocks crop out in places ".

This indicates mineral country, but Winnecke was not above calling a red quartzite a granite, as in the case of the Keepera Ridges. The area marked Adam Ranges on Winnecke's map is the area to prospect, the broken country at the headwaters of the Field River, round Alanajeer, and westward to the Tarlton Range.

East of the Adam Ranges and the Toko Range, sandy desert stretches across to the Mulligan, which brings us back to the starting point in our description of the environs of the Simpson Desert.

When I returned from my aerial reconnaissance in 1929 I said that there was nothing to warrant the expenditure of any further human effort in the exploration of the Simpson Desert; that nothing lay within its borders other than is to be seen round its margins; and my further investigations and enquiries have tended to confirm that view. Yet there is great satisfaction in any physical achievement, in the overcoming of natural obstacles, in treading where no man has trod before. Mt. Everest has been photographed from the air; we know all we want to know about it; yet man must put his foot on the summit. The middle of the Simpson Desert must be crossed; opals may still be there; the vegetation probably does not vary, and we know the edges, but a botanical cross section systematically done would be of great interest. There are two routes that suggest themselves: one, from west to east, by starting from Andado Bore and going north-east over easy country to the Hale-Todd junction, over Day's route, and then eastward along the 25th parallel to Winnecke's waterhole on the Mulligan, or the Woolcanare Bore. This is a total of 230 miles, the first 50 miles of which is easy going, the last 190 crossing sandhills nearly at right angles. Fifteen days is a fair estimate of the time required. Good camels, after a wet season when feed was fresh, would not require water, and there would be no water on this route. Well-tried working camels are essential. The distance is nothing; it is the crossing of the sand-ridges that tells on the camels. They frequently have to struggle over the crests on their knees.

Another interesting journey would be a north-south crossing. The route for this would be from Alice Springs down the Todd to latitude 24°, then eastward to the 136th meridian, then due south-east to Poeppel's Corner. In a good season water would be found in the Hale. The distance between waters would be forty miles to the 136th meridian, then 186 miles to Poeppel's Corner, twenty-five miles short of which Perlanna native well should be struck, or twenty miles short, Poolaburda native well. This course runs parallel to the sand-ridges and would present little difficulty. Twelve days should bring one to Poeppel's Corner, with another three days for the sixty miles to Alton Downs Station. The second and longer journey would probably prove the easier. Long stages could be done if the necessity arose, and the time be halved.

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EXPLANATION TO PLATES.

(Except where otherwise stated, photos are by the author.)

Plate IV.

The Simpson Desert and Its Environs.

Plate V.

Above.—Low mesas of the Eyrean beds a few miles north of Birdsville, on the east side of the Simpson Desert. The foreground shows the top of a flat-topped hill, with the siliceous crust broken into boulders, the first stage in the formation of gibbers, with which the plains are strewn, and the principal origin of the sand. Looking north-east.

Below.—Typical country to the north of the Simpson Desert on the track to Tobermory, east of the Tarlton Range. Spinifex, mallee and mulga.

Plate VI.

Above.—The course of the Mulligan, west of Birdsville, looking south. Several deserted channels can be seen. Note parallelism with the sand-ridges. Aerial, 4,000 feet.

Below.—The south-eastern margin of the Simpson Desert, which begins at Goyder's Lagoon in the background; this view is right on Sturt's route into the Desert. The straggly nature of the sand-ridges is typical of the southerly borders of the Desert. Looking south-east. Aerial, 5,000 feet.

Plate VII.

Above.—Typical sand-ridges of the interior of the Desert showing their parallelism. The bottom of the picture is a mile across. Barren country. Aerial, 3,400 feet.

Below.—A single sand-ridge in the south-west corner of Queensland, between the Mulligan River and the Territory boundary. The dark patches are spinifex and cane-grass, and the trees small acacias. Aerial, 4,000 feet.

Plate VIII.

Above.—The head of Phillipson's Creek, typical of the country on the north-west side of the desert south of the MacDonnells. As in the MacDonnells, the streams are antecedent and cross the ranges. Aerial, 3,000 feet.

Below.—A sand-ridge on the 26th parallel, north of Lake Eyre, looking south. The steepness on the east side is well seen and is general throughout. The aboriginal is wearing a " sack " suit. (Photo.—E. A. Colson.)

Plate IX.

Above.—Barren gibber plains at Abminga, on the west side of the desert, 1936.

Below.—The same type of country as above after heavy rains, 1937.

Plate X.

Above.—A range on the west side of the Todd, ninety miles from Alice Springs, against which the long sand-ridges of the desert end. The desert stretches in an unbroken plain between this point and Birdsville, 300 miles away, but there are many ridges and broken country between this point and the MacDonnell Ranges. Aerial, 3,800 feet.

Below.—Flat-topped hills on the margin of the desert north of the Finke and east of Rumbalara, looking east. These are probably composed of Finke River sandstone. Aerial, 1,000 feet.

Plate XI.

Above.—Looking south into the Simpson Desert from the south end of the Tarlton Range. The gum tree-lined course of the Hay may be seen in the background.

Below.—Taking a soil sample in the north end of the desert, ten miles south of the Tarlton Range. Spinifex and mallee.

THE DIMORPHISM OF BISPYRIDINE COBALTOUS CHLORIDE.

By D. P. Mellor, M.Sc.,
and B. S. Morris.

(*Manuscript received, November 20, 1937. Read, April 6, 1938.*)

Two substances differing in crystalline form and other physical properties but identical in empirical composition may be:

(1) Dimorphous.
(2) Isomeric.
(3) Polymeric.

In the last instance molecular weight determinations usually decide at once whether one substance is a polymer of the other or not. The proof that two substances of identical empirical composition are isomeric is generally based on the detection and elucidation of differences in their chemical reactions, unless the substances happen to be enantiomorphous forms, when their behaviour towards polarised light is possibly their most significant difference. It may occasionally happen that, either only very small chemical differences[1] exist between two isomers, or that no suitable means have been devised for detecting the differences. In cases such as these a distinction between the possibility of the two substances being either isomeric or dimorphous may be effected by physical means.[2]

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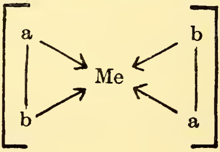
[1] Geometrical isomers of internally complex compounds of the type



particularly those in which all bonds to the central metal atom are the same, and where cistrans isomerism arises from the square coordination of the unsymmetrical chelate groups may exhibit but small differences in chemical behaviour.

[2] See "Crystalline Form and Chemical Constitution", Tutton, Macmillan, 1926.

It is considered that polymorphism in molecular crystals, for example, arises from different modes of packing of molecules in the crystal lattice. In regard to the conditions determining the different packing modes the view recently put forward by Buerger and Bloom (*Zeit. für Krist.*, 1937, *96*, 182) may be quoted: "The arrangement of the molecules in molecular crystals may therefore often be expected to be conditioned by the space requirements best adapted to 'outer' vibration modes. Transitions may accordingly be expected between different structures of identical molecules in different packing arrays each adapted to different vibration types." This being the case, solutions of dimorphous substances in the *same solvent* should be identical. For example, no differences have been reported between carbon disulphide solutions of monoclinic and rhombic forms of sulphur, the dimorphism of which is well established. On the other hand solutions of isomers which are not so readily interconvertible as to be classed as tautomers may be expected to differ, among other things, in absorption spectra, a difference which, in the case of coloured substances, lends itself more readily perhaps than any other to eliminating the possibility of dimorphism. The solute molecules of isomers, in contrast with those of dimorphs, may be expected to exhibit different Raman spectra, refractive indices, and dipole moments, etc.

THE VIOLET AND BLUE FORMS OF BISPYRIDINE COBALTOUS CHLORIDE [$CoPy_2Cl_2$].

These substances have been described by Hantzsch (*Zeit. für anorg. Chem.*, 1927, *159*, 273) as isomeric. The isomerism was considered to arise from a cis and trans planar distribution of pyridine and chlorine about the cobalt atom. Since Co^{II} is not among the metals listed by Pauling for which square coordination may be expected, it was thought worth while reexamining the above substances. Not long after commencing this work Sugden (*Nature*, 1937, *139*, 375) reported magnetic data for each form. In the same communication it was indicated that molecular weight determinations and conductivity data for each of the two forms had already been published. As we were unable to find this information in the references given, the work was proceeded with.

Experimental.

The two forms were prepared in the manner described by Hantzsch (*loc. cit.*), but it was found necessary to precipitate the blue form from boiling bromoform solution, a procedure which indicated that the transition point between the two forms was in the neighbourhood of 120° C. The behaviour of the violet form on being heated in the dry state confirmed this.

Analysis.

Violet form: (α) Co=20·25% Cl=24·8%.
Blue form (β) Co=20·1% Cl=24·9%.
$CoPy_2Cl_2$ requires Co=20·49%, Cl=24·6%.

On heating the violet form to 120° C., it darkened and changed to the blue form, which subsequently melted at 196°. On heating the blue form no change in colour takes place, but it melts to a liquid at 195° C.

In bromoform the molecular weights of both forms (determined cryoscopically) were identical within the limits of experimental error.[3] Violet form=318; blue form=302; theoretical=288. One form is therefore not a polymer of the other. Bromoform solutions of the two forms possessed *identical absorption* spectra. In order to make certain of this point solutions of the blue form were freshly made up for this test, and even examined while the substances were dissolving lest a rapid transition should be overlooked. No differences could be detected. In bromoform solution neither form showed any appreciable electrolytic conductivity. The conductivity of both forms was measured during the process of solution in order to detect a possible change of conductivity with time. None was

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[3] These values agree with those published by Cox, Shorter, Wardlaw and Way (*Journ. Chem. Soc.*, 1937, 1556) in a paper which has appeared since the completion of the work described above. These authors consider that, in view of the differences of colour and magnetic properties of the two substances, it is unlikely that they are dimorphous. On the strength of the fact that the distance between Co atoms in the violet form is 3, A. V. Cox and his collaborators suggest that there is a planar arrangement of bonds about cobalt atom in this form. This is not necessarily in conflict with the view that the α and β forms are dimorphous.

It should be pointed out that the results of the magnetic measurements made by Sugden (*loc. cit.*) on both forms of bispyridine cobaltous chloride are inconsistent with the value predicted by Pauling (*J. Am. Chem. Soc.*, 1931, *53*, 1367) for square coordinated Co^{II}. Magnetic measurements on bispyridine manganous chloride are planned to test this case as well.

observed. Nor could any appreciable change in conductivity be observed during the heating of the bromoform solution to 135°. The blue form cannot be $[CoPy_4][CoCl_4]$ as has been suggested (Sugden, *loc. cit.*), since if it were unionized in bromoform solution, as it would have to be (see conductivity data above), the molecular weight should be double that observed. Actually the observed molecular weight is normal.

Both methyl alcohol and aqueous solutions of the two forms were pink in colour, in definite contrast to the blue of the bromoform solutions. The molecular conductivity of N-500 ethyl alcoholic solutions of each form was $320w^{-1}$. This and the instantaneous and complete precipitation of AgCl on treating alcoholic solutions with silver nitrate indicate that the substances can function as salts as well as non-electrolytes :

(*a*) $[CoPy_2Cl_2] \rightarrow [CoPy_2]^{++} + 2Cl^-$.
(*b*) $[CoPy_2Cl_2] + 2C_2H_5OH \rightarrow [CoPy_2(C_2H_5OH)_2]^{++} + 2Cl^-$
(*c*) $[CoPy_2Cl_2] + 2H_2O \rightarrow [CoPy_2(H_2O)_2]^{++} + 2Cl^-$.

In connection with the possibility (*b*), it should be pointed out that $[CoPy_2Cl_2]$ may be recrystallised from ethyl alcohol. All attempts to observe differences in the chemical behaviour of the two forms gave negative results. Summing up, it may be said that the evidence favours the view that the blue and violet forms of bispyridine cobaltous chloride are dimorphous, and that it is unnecessary to postulate cis-trans isomerism of square coordinated Co^{II} to explain their occurrence.

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TEMPERATURE AND SPECIFIC GRAVITY OF SEA-WATER BETWEEN JAPAN AND AUSTRALIA. TRANSCRIPTION OF OGURA'S FIGURES.

By Marcel Aurousseau, M.C., B.Sc.

(Communicated by E. C. Andrews.)

(Manuscript received, December 15, 1937. Read, April 6, 1938.)

Between July 12th and September 17th, 1923, Captain S. Ogura, of the Nippon Yusen Kaisha, made a systematic series of observations of the temperature of the air and sea, and of the specific gravity of the surface-waters, on the run from Nagasaki to Sydney and back. His results, published in Japanese, in the *Journal of Geography* (Tokyo),[4] have been neglected.

Thanks to an admirable handbook by Koop and Inada,[3] the transcription of columns of Chinese and Japanese figures is no longer a difficult task. I have therefore transcribed Captain Ogura's tables, and present them substantially in their original form, as follows:

TABLE 1.

Date (1923).	Hour.		Latitude.		Longitude.		Temp. (Air).	Temp. (Sea).	Sp. Gr., 15/4 C.
			°	′	°	′	° C.	° C.	
July 12	18	0	N. 33	23	E. 129	22	24·0	22·5	1·0258
14	8	26	31	12	127	40	—	25·0	1·0230
14	18	26	29	48	125	55	24·0	25·1	1·0226
15	8	44	27	37	123	14	25·2	27·1	1·0250
15	18	44	26	17	121	25	25·6	26·8	1·0258
16	9	0	24	25	118	56	26·9	27·4	1·0244
16	19	0	23	7	117	10	27·9	27·2	1·0249
17	8	0	22	15	114	26	28·3	26·8	1·0208
18	19	0	21	23	115	12	29·5	29·5	1·0215
19	9	0	19	5	117	2	28·8	28·5	1·0248
19	19	0	17	9	118	20	29·6	28·9	1·0252
20	9	0	15	8	119	45	26·4	27·6	1·0240
20	14	20	14	24	120	28	28·1	28·5	1·0201
21	19	0	13	47	120	30	28·5	27·8	1·0234
22	9	0	11	15	121	26	28·5	28·2	1·0246
22	19	30	9	12	121	50	28·8	28·6	1·0248
23	19	0	5	55	122	42	28·3	28·2	1·0252
24	8	48	3	32	124	2	28·2	28·2	1·0252
24	18	48	1	50	125	17	26·8	27·7	1·0252
25	8	38	S 0	30	126	20	27·2	27·0	1·0252
25	18	38	2	12	127	0	26·9	26·9	1·0258
26	8	28	4	27	128	36	25·3	26·0	1·0251
26	18	28	5	32	130	17	25·2	25·0	1·0255
27	8	7	6	58	132	42	24·7	25·0	1·0252
27	18	7	7	33	134	14	24·7	24·2	1·0256

TABLE 1.—*Continued.*

Date (1923).		Hour.		Latitude.		Longitude.		Temp. (Air).	Temp. (Sea).	Sp. Gr., 15/4 C.
				°	′	°	′	° C.	° C.	
July	28	7	51	8	53	136	25	25·2	24·7	1·0252
	28	17	51	9	37	138	22	24·6	25·0	1·0253
	29	7	0	10	34	140	50	23·6	23·7	1·0264
	30	7	0	11	53	143	14	22·5	22·7	1·0264
	30	17	0	13	31	143	40	23·2	23·4	1·0267
	31	7	0	15	2	145	40	22·5	22·3	1·0262
	31	17	0	16	45	145	50	21·8	22·5	1·0260
Aug.	1	9	0	19	2	146	58	21·4	21·0	1·0266
	1	17	0	19	41	148	8	20·7	21·4	1·0266
	2	6	30	21	21	150	0	19·2	20·2	1·0267
	2	16	30	22	24	151	17	20·0	20·4	1·0266
	3	6	30	24	7	152	48	17·1	21·2	1·0264
	3	16	30	25	43	153	27	18·0	20·3	1·0263
	4	16	0	27	0	153	25	14·8	18·3	1·0263
	5	6	30	29	34	153	36′	12·7	19·1	1·0264
	5	16	0	31	48	152	59	11·2	18·3	1·0265

TABLE 2.

Date (1923).		Hour.		Latitude.		Longitude.		Temp. (Air).	Temp. (Sea).	Sp. Gr.; 15/4 C.
				°	′	°	′	° C.	° C.	
Aug.	22	7	0	S. 30	53	E. 153	7	17·5	18·5	1·0265
	22	16	30	29	9	153	33	21·6	18·6	1·0266
	23	6	0	27	11	153	20	18·0	19·3	1·0266
	24	16	30	26	31	153	21	21·6	20·6	1·0266
	25	6	0	24	21	153	13	21·4	21·6	1·0264
	25	16	30	22	56	151	52	21·7	21·2	1·0264
	26	6	0	21	13	149	54	22·1	22·3	1·0265
	26	16	30	19	53	148	23	23·2	23·2	1·0265
	27	6	0	18	17	146	28	22·2	23·8	1·0265
	27	16	30	16	31	145	42	24·0	24·4	1·0263
	28	6	0	14	22	144	42	22·3	24·1	1·0264
	28	16	30	13	5	143	36	24·2	25·0	1·0264
	29	6	0	10	52	142	24	24·7	25·1	1·0268
	29	16	30	10	40	141	26	26·0	25·5	1·0265
	30	6	36	9	46	138	55	25·0	25·0	1·0259
	30	17	6	8	59	136	57	25·5	25·2	1·0255
Sept.	1	6	56	7	43	134	23	24·4	25·4	1·0255
	1	17	26	6	45	132	29	26·0	26·4	1·0251
	2	7	14	5	27	130	10	25·5	26·7	1·0257
	2	17	44	4	11	128	26	27·4	27·1	1·0255
	3	7	23	1	57	126	50	26·5	26·6	1·0257
	3	17	53	0	9	126	3	27·2	27·4	1·0253
	4	7	32	N. 2	12	124	57	27·5	28·5	1·0254
	4	18	2	4	3	123	57	28·5	28·5	1·0254
	5	8	0	6	24	122	25	26·5	27·2	1·0250
	5	18	30	7	0	121	54	26·5	27·8	1·0242
	6	8	0	9	35	121	51	27·2	27·7	1·0240
	6	18	30	11	14	121	22	27·5	28·1	1·0238
	7	8	0	13	20	120	17	27·5	28·0	1·0236
	8	18	30	15	0	119	53	27·3	28·4	1·0240
	9	8	0	16	55	118	37	26·7	27·8	1·0244
	9	18	30	18	19	117	30	25·8	27·1	1·0245
	10	8	0	20	3	116	14	25·3	27·4	1·0240
	10	18	30	21	30	115	7	24·5	26·5	1·0249
	11	18	30	22	14	114	21	23·3	26·0	1·0232
	12	8	0	22	48	116	47	20·9	23·8	1·0242
	12	18	30	23	55	118	33	21·5	23·1	1·0243
	13	7	40	25	21	121	5	23·1	23·6	1·0253
	13	18	10	26	10	123	0	22·6	23·6	1·0249
	14	7	20	27	52	125	8	23·0	23·1	1·0253
	14	17	50	29	30	126	47	21·0	24·5	1·0260
	15	7	0	31	35	128	43	21·5	25·2	1·0256
	16	7	0	33	53	130	19	17·5	21·0	1·0253
	16	17	30	33	44	132	19	20·3	21·8	1·0242
	17	6	30	34	29	134	35	16·8	22·0	1·0226

Considering only the results obtained south of the equator, I find that Ogura's figures are in close agreement with what is already known about the temperature,(2, 5, 6) and the specific gravity(1, 2, 5, 7, 8) of the waters off eastern and northern Australia between July and September. Captain Ogura's figures could, therefore, be accepted with confidence, even though his reputation as a physicist were not, as it is, firmly established. So few are the adequate records of this kind that these neglected figures are an important addition to our knowledge of Australian waters.

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AN X-RAY EXAMINATION OF CHILLAGITE.

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(*Manuscript received, February 7, 1938. Read, April 6, 1938.*)

The morphology of chillagite has been studied by Smith and Cotton.[1] The substance is found in translucent, yellow, tetragonal crystals of tabular habit at Chillagoe, Queensland. A formula $PbMoO_4 . PbWO_4$ was at first assigned, but later analyses correspond very approximately to the formula $3PbWO_4 . 5PbMoO_4$. Smith and Cotton, finding many of the crystal forms common to chillagite, stolzite and wulfenite, concluded that the three substances were definitely related; but a $\frac{c}{a}$ ratio of 1·5291 for chillagite, lower than that of wulfenite (1·5771–1·5774) or stolzite (1·5576–1·5692), was put forward as evidence in favour of chillagite being regarded as a new mineral. In calculating the $\frac{c}{a}$ ratio, ρ values of the form {115} were averaged, and the intercepts on the crystallographic axes of the unit form calculated from this mean ρ. The crystals examined were imperfect and incomplete, but this {115} form was present on all crystals studied except one.

The imperfection of the chillagite crystals may be judged by studying Smith and Cotton's table.(1) Variations in φ values of faces in the $[1\bar{1}0]$ zone, from 44° 1′ to 46° 0′, show what poor crystals are available for examination. The ρ values of the (115) faces range from 23° 7′ to 24° 20′ in the crystals measured. Because this plane is complex, these limiting ρ values would give to the crystal, $\frac{c}{a}$ ratios of 1·5092 and 1·5988 respectively. (Ten minute differences in this angle affects the second decimal place of the $\frac{c}{a}$ ratio.)

The averaging of $001 \wedge 115$ interfacial angles on such imperfect chillagite crystals has resulted, unfortunately, in a $\frac{c}{a}$ ratio which is misleading. The comparison of interfacial angle measurements in wulfenite, chillagite and stolzite noted below, indicates close similarity. Discrepancies for chillagite from values intermediate between stolzite and wulfenite are not remarkable on such imperfect crystals.

	$001 \wedge 111$	$001 \wedge 011$
Wulfenite	65° 51′	57° 37′
Chillagite..	64° 40′–65° 54′	57° 16′, 58° 42′*
Stolzite	65° 37′	57° 21′

The specific gravity of chillagite is intermediate between the values recorded for wulfenite and stolzite. The values are as follows: wulfenite (6·7–7·0),(2) chillagite (7·3),(1) stolzite (7·87–8·13).(2)

Stolzite and wulfenite have been subjected to X-ray examination by several workers.(3, 4, 5, 6, 7, 8) These minerals are now recognised as members of the scheelite group(7, 8) of isomorphous compounds (XLO_4), where K=Ca, Ba, or Pb, and L=W or Mo, with space-group C_4^6h.

Chillagite was investigated by the standard powder and oscillation methods, using copper (Kα) radiation and a cylindrical camera of radius 3 cm. The following unit cell dimensions were obtained: $a_0 = 5{\cdot}43$Å, $C_0 = 12{\cdot}08$Å (mean values).

From these values, the volume of the unit cell, assuming the formula to be $3PbWO_4 . 5PbMoO_4$, is 356 Å^3, and the number of molecules per unit cell is 3·94, i.e. 4. In the table below, cell dimensions of wulfenite, stolzite and chillagite are compared.

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* The $001 \wedge 011$ angle calculated from the $\frac{c}{a}$ ratio of 1·5291 is 56° 49′, a smaller angle than either of those obtained experimentally.

	Wulfenite $PbMoO_4$.	Chillagite $3PbWO_4 . 5PbMoO_4$.		Stolzite $PbWO_4$.
	1	2	3	4
a (Å)	5·41	5·41	5·46	5·44
c (Å)	12·08	12·08	12·11	12·01
$\frac{c}{a}$	2·23	2·23	2·22	2·21
No. of molecules per unit cell..	4	4	4	4

Results for chillagite in column 2 were obtained from a powder photograph; results in column 3 were calculated from oscillation photographs about the symmetry axes. Experimental difficulties with imperfect crystals were responsible for a lower order of accuracy of these latter measurements.

It is obvious that the $\frac{c}{a}$ ratios in the table are not comparable with the crystallographic ratios for the substances concerned, owing to the fact that the " a "-axis of the unit cell is 45° removed from the " a " crystallographic axis.

Some of the earlier X-ray investigators(3, 5, 6) of scheelite type crystals regarded a larger cell of 8 molecules as the unit. On structure grounds(7, 8) this large cell is rejected, but it is interesting to note the close agreement between the identity period along the " a " crystallographic axis (really the cell side diagonal) in chillagite crystals with that of stolzite and wulfenite.

Stolzite(6)	..	a=7·69 Å
Chillagite	..	a=7·68 Å
Wulfenite(6)	..	a=7·65 Å.

With close agreement in cell dimensions, and the same number of molecules per unit cell, identical ionic radii for molybdenum and tungsten* preclude the possibility of a structure unique from that of the H_4 type of stolzite and wulfenite for a mixture of lead tungstate and lead molybdate.

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* Mo=0·68 Å, W=0·68 Å (Goldschmidt).
Mo=0·66 Å, W=0·66 Å (Pauling).

SUMMARY.

After critically examining the crystallographic data and carrying out a partial X-ray analysis, the authors are therefore of the opinion that chillagite is not a distinct mineral species.

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STUDIES ON PHYSIOLOGIC SPECIALISATION OF THE ORGANISMS CAUSING BUNT IN WHEAT, AND THE GENETICS OF RESISTANCE TO THIS AND CERTAIN OTHER WHEAT DISEASES.

PART II. GENETICAL STUDIES.[1]

By J. G. CHURCHWARD, Ph.D., B.Sc.Agr.

(With Plates XII-XIII, and three text figures.)

(Manuscript received, February 22, 1938. Read, April 6, 1938.)

1. REVIEW OF LITERATURE.

Bunt.

Farrer[25] was the first worker to breed wheat specifically for bunt resistance. He produced two highly resistant varieties, Florence and Genoa,[58] but did not attempt a genetic study of the inheritance of resistance.

In 1905 Biffen[5] showed that resistance to yellow stripe rust (*Puccinia glumarum* Erikss.) behaves as a simple Mendelian recessive character. Since that time it has been demonstrated that resistance of plants to many diseases is inherited in a Mendelian fashion.[39]

Gaines[30] was the first investigator to record the mode of inheritance of resistance to bunt of wheat, and considered that, if the resistance was inherited on Mendelian lines, it was due to multiple factors. He maintained that some varieties, such as Hybrid 128 and Jones' Fife, possessed no factors for resistance, while others had two or three, each reducing the amount of bunt by 10–15 per cent. Fortyfold, Red Russian, and Marquis possessed one or a few factors which brought about a 10–25 per cent. reduction,

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[1] Submitted to the Faculty of the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The work was carried out at Hawkesbury Agricultural College, N.S.W., and at the University of Minnesota during the writer's tenure of the Walter and Eliza Hall Agriculture Research Fellowship, Sydney University. For the facilities provided the author expresses his gratitude to the authorities concerned.

while Florence possessed several factors which reduced the amount of bunt by 70 to 75 per cent. when compared with susceptible varieties.

In crosses between immune and susceptible varieties, resistance was found to be dominant, but when a resistant variety like Florence was crossed with a susceptible variety, susceptibility was dominant.

Gaines and Smith(32) have demonstrated a single factor difference between White Odessa and Hohenheimer for resistance to two physiologic races of bunt. Hybrids of these two varieties, however, reacted differently to the third physiologic race, indicating a two factor difference.

In a cross between Martin and Hard Federation, Briggs(7) showed that there is a single factor difference for resistance. In further investigations(8), (11), (13) he demonstrated that the resistance of White Odessa, Banner Berkeley, Odessa and Sherman results in each case from the same dominant factor which is identical with that carried by Martin.

He further demonstrated that Hussar(10) differs from susceptible varieties, such as Baart, by two factors, one being identical with that possessed by Martin, the other, designated as the Hussar factor, allowing the development of bunt in 50 per cent of the heterozygous families. Selections 1418 and 1403, made by Briggs, each possess only the Hussar factor.

Two strains of Turkey were shown to differ from White Federation by a single factor for resistance,(12) which, although similar in its effect, is different from the Hussar factor. The factor for resistance in Oro(14) was identified as this Turkey factor. Thus Briggs has demonstrated the presence of three major factors which are dominant for resistance to bunt. These have been designated the Martin, Hussar, and Turkey factor and are different from the single recessive factor possessed by Florence.(16)

Briggs(9) further found that modifying factors may influence the resistance of a variety to bunt. From a cross between Hussar (resistant) and Hard Federation (susceptible), strains were isolated which bred true for a small percentage of bunt infection.

Aamodt(3) studied the inheritance of resistance to bunt in F_3 families of crosses made between the various combinations of resistant, moderately susceptible, and susceptible varieties of wheat. He found transgressive segregation and assumed that multiple factors, whose exact nature was not determined, governed resistance to bunt.

Bressman and Harris(6) have found that Albit differs from Hybrid 128 by a single dominant factor for resistance, which is the same as that possessed by its male parent, White Odessa.

Kilduff(50) made studies in the inheritance of resistance to bunt in Red Bobs and Garnet crosses with Kota, which indicated the presence of several dominant factors for resistance.

Clark, Quisenberry, and Powers(22) studied the reaction to bunt in three crosses with Hope wheat. Their results indicate that the stronger the degree of resistance the less complicated is the inheritance. Several factors for resistance were postulated.

In Australia, Churchward(16) has shown that there is a single factor difference with dominance of susceptibility, between Florence (resistant) and susceptible varieties of wheat, viz. Hard Federation, Firbank, Gullen, Marshall No. 3, and Yandilla King. This is apparently different from the three dominant factors for resistance demonstrated by Briggs, and is the fourth factor known up to the present.

Rust.

The number of investigations made on the nature and inheritance of resistance to stem rust of wheat caused by *Puccinia graminis tritici* E. & H., is very considerable. Only those pertaining to the problem will be reviewed.

Hayes(43) summarised previous work in the nature and inheritance of resistance to stem rust of wheat, indicating its influence on our present viewpoint of breeding desirable disease resistant varieties.

That the fungus causing the stem rust of wheat consists of many physiologic races which differ in their ability to infect certain wheat varieties has been shown by Stakman *et al.*(63), (64)

This would explain why varieties hitherto resistant may suddenly become susceptible, and why one resistant wheat transferred to a different geographic region may become susceptible. Hence in studying the genetics of resistance to rust it is necessary to know what races are present.

Many investigations(1, 2, 34, 36, 41, 42, 44, 47, 48, 51, 53, 59) have shown that resistance to stem rust in seedling stage, to a single or group of physiologic races, may be determined by a single genetic factor.

Hayes and Aamodt,(44) Hayes *et al.*(48) working with Race 2, found that there was no correlation between the seedling and field reaction in Marquis × Iumillo and Kota × Marquis crosses. Certain lines, susceptible as seedlings, showed resistance at maturity.

Similar results were obtained by Quisenberry(59) in H 44 × Minhardi crosses, with Races 36 and 60. Goulden *et al.*(36) and Neatby and Goulden(54) studied the seedling reaction of H44 × Marquis cross to Races 21 and 36 and concluded that two factors determined the reactions to Race 36. They also concluded from this study that different genetic factors controlled resistance in the field. They explained their results on a single factor basis. Clark and Ausmeus,(19) however, found that two factors determined resistance in the field in Hope, Marquis and Reliance crosses. Neatby and Goulden(54) obtained similar results with a Marquis × Hope cross.

Harrington(40) studied the reaction of Marquis, Pentad, and Mindum to Races 34 and 21 of stem rust in seedling and mature plant stages and found a general agreement between the field and greenhouse reactions.

Seedling and mature plant reactions to sixteen different physiologic races of rust were studied by Goulden, Newton and Brown.(37) They concluded, on the basis of the results obtained, that the fourteen varieties tested could be divided into 3 groups: (i) where there was good general agreement between seedling and mature plant reactions; (ii) where there was lack of agreement; (iii) a group intermediate between (i) and (ii). Hope was resistant to all 14 Races in the field, but in the seedling stages was susceptible to 6, viz. Races 9, 15, 17, 21, 32, and 34.

Papers dealing with the mode of inheritance of the other characteristics concerned in this cross are briefly reviewed under their respective headings.

2. Materials and Methods.

Bunt.

In 1927 a wheat cross, Federation × Hope, was made at the University of Sydney. The F_1 generation was grown in 1928, eight of the crossed grains being inoculated with spores of *T. tritici*. Others were surface sterilised and sown without being inoculated. Each F_1 plant was harvested separately. A portion of the harvest was kept; the other part was sown uninoculated and harvested as F_2 in 1929. In this way F_2 and F_3 grain was available for sowing at one time, both generations being subjected to the same environmental conditions in testing their reaction to bunt. The F_2 plants produced on the average approximately 300 grains, which allowed a number of tests to be made in the F_3.

In late June, 1931, the F_2 and F_3 generations were sown at the Hawkesbury Agricultural College, Richmond, New South Wales, Australia. The sowing of the block was completed within a day in order to minimise any effects from changing soil conditions.

In April, 1932, 766 strains, representing 27 families from the " homozygous " resistant group of the F_3 generation, were sown at University Farm, St. Paul, Minnesota, U.S.A. Grain of nine of these F_4 families was sown at Richmond, N.S.W., in 1933. Each family contained approximately 40 plants, and the progeny of a single plant occupied one row.

The grains always were sown by hand two inches apart in rows 10 feet long and 8 inches apart.

Fresh viable spores of *T. tritici* were used to inoculate the grain, which was shaken just prior to planting, with an excess of inoculum until thoroughly blackened. The inoculum was originally obtained from Dr. W. L. Waterhouse, Sydney University, in 1927, and since that time has been increased annually by growing on Federation wheat. The collection comprised one physiologic race of bunt known as Form N1.

Each plant was harvested separately and placed in one of three groups: (i) bunt free, (ii) plants showing " late tiller " infection, (iii) bunted. Hope, the resistant parent, showed a low percentage of " late tiller " infection which is regarded as resistant. This refers to a type of resistance where only the fifth or sixth tiller is found to be bunted and the yield of the plant is apparently affected very slightly. The degree of infection is expressed as a percentage of infected plants per row. Gaines(30) made a quantitative estimate of the bunt present in each row, according to the formula $ab+c=d$. In this formula a is the percentage of bunted heads on partly bunted plants, b is the percentage of partly bunted plants in the row, c is the percentage of entirely bunted plants in the row, and d is the total percentage of bunted plants in the row. While this is a satisfactory quantitative measure of susceptibility, each plant ceases to be regarded as a genetic entity, and, therefore, as Briggs(7) points out, it may not be the best method for indicating segregation within the row.

In this study, if a plant is wholly or partially infected, except in the case of " late tiller " infection, it is regarded as susceptible.

Rust.

Field notes were taken on the occurrence of stem and leaf rust. The types of infection ranged from " 0 " to " 4," " 0 " indicating immunity and " 4 " complete susceptibility. The intermediate degrees of development of these types are indicated by + and — signs. An explanation of the types is set out below.

Susceptible classes. Type " 4." Complete susceptibility, large confluent urediosori without signs of hypersensitiveness.

Type " 3." Susceptibility, infection fairly heavy, urediosori coalescing though not confluent, no signs of hypersensitiveness.

Resistant Classes. Type " 2." Moderate resistance, infection light, urediosori small. A necrotic ring encloses the pustule in a small green island.

Type " 1." High resistance, infection very light, urediosori small and scattered, surrounded by sharp necrotic areas.

Type " 0." Immunity, no urediosori, small well defined, supersensitive flecks may develop.

The F_2 plants were classified as susceptible or resistant, and the F_3 families were homozygous or heterozygous for susceptibility and for resistance.

In the greenhouse, F_3 remnants were tested for their reaction to two races of stem rust, viz. 33 and 34. Approximately 20 plants were sown in the pots. The seedlings. were inoculated, incubated for 48 hours in a moist chamber and then allowed to develop in the greenhouse at temperatures varying from 20° to 22° C.

There was no difficulty in separating the homozygous and heterozygous classes when Race 33 of stem rust was used. However, with stem rust Race 34, under the prevailing greenhouse conditions, Hope, the resistant parent, showed a 3-cn reaction. The urediosori which could not be mistaken for the large 4+ pustules of Federation developing under the same conditions, were considerably smaller and surrounded by a sharp continuous necrotic area with a chlorotic border. The 4+ pustules of Federation showed no signs of hypersensitiveness. Certain of the plants showing the " Hope-type " of reaction were transplanted from the greenhouse into the field at the University Farm, St. Paul, in 1932, and proved resistant to stem rust. The families were divided into three classes: (*a*) homozygous susceptible; (*b*) homozygous for Hope type of reaction; (*c*) heterozygous.

Flag Smut.

Further remnants were tested for their reaction to flag smut. The inoculum, which was obtained by crushing infected flag of wheat, was floated on water in open petri dishes and allowed to soak for 48 hours. The grain was then added, and after soaking for 8 hours, approximately 30 grains were sown in 10 inch pots. The soil was kept just moist enough to allow for the germination of the grain, until the first leaf had well developed. The soil was kept at a temperature of 21° C. throughout the experiment. The first signs of infection appeared on the 4th and 5th leaves about 40 days after inoculation. The percentage of infection was estimated on the number of plants infected compared with the total number in the pot. It is possible that some seedlings may have been killed before emergence from the soil, but no attempt was made to estimate the number of plants so affected.

Morphological Characters.

(*a*) Emergence of First Leaf and Colour of Coleoptile.

In conjunction with the rust and flag smut tests in the greenhouse, coleoptile colour and time of emergence of the first leaf from the coleoptile were studied. Families were classified as homozygous or heterozygous for earliness or lateness in leaf emergence, as well as for purple or green colour of the coleoptile.

(*b*) Awns.

The F_2 plants and the F_3 families were carefully separated into five awned classes, as proposed by Clark, Florell and Hooker,(20) viz.: (i) awnless, (ii) apically awnletted, (iii) awnletted, (iv) short awned, (v) awned.

Segregating F_3 families and F_4 strains were separated into similar groups, and their mode of behaviour was noted.

(*c*) Habit.

Under Australian conditions Hope is prostrate in its early habit of growth; Federation is erect. F_2 plants were either erect, prostrate, or intermediate in growth habit, and the F_3 generation was classified as homozygous erect and prostrate or heterozygous.

(*d*) Straw Colour.

Hope has a purple straw colouration which is absent in Federation. Plants in the cross were considered either as purple or white, no attempt being made to note intermediacy.

(*e*) Maturity.

The dates of heading out of the F_2 and F_3 generations were noted. All plants maturing as early as Federation and as late as Hope were placed in their respective bundles, and the remainder were classified as intermediate. The F_3 families were classified as early, early-midseason, midseason, midseason-late, and late.

(*f*) Grain Colour.

The F_2 plants were separated according to grain colour into five classes: (class 1) white, (class 2) near white, (class 3) intermediate, (class 4) near red, (class 5) red. The F_3 families were classified into 5 classes according to their mode of segregation.

Associations.

The interrelations of the various characters were studied. The measure of independence of reaction between all the possible paired combination of characters was determined by calculating the χ^2 for independence and interpolating for a P value from Fisher's table.(27) The number of degrees of freedom was calculated from $n=(r-1)(c-1)$ for a contingency table with r rows and c columns. No attempt was made to measure the degree of association.

In comparing the class frequencies obtained with those expected in the various Mendelian ratios, the χ^2 for goodness of fit was calculated and $P=0\cdot05$ was taken as the minimum level of significance.

Parental Stock.

Both of the varieties used in the cross discussed in this paper are common wheats (*Triticum vulgare* Host.). Federation is a popular wheat grown in Australia and certain sections of the Pacific north-west of the United

States. It is high yielding and drought resistant, but is highly susceptible to all the diseases herein discussed. It has white grain and the straw has no purplish colouration. The brown chaff is bald and the plants mature, under Australian conditions, earlier than Hope.

Hope, the result of a cross between Yaroslav Emmer and Marquis, has outstanding stem and leaf rust resistance in the field. In addition, it is resistant to flag smut and bunt. The head is fully awned, with a light chaff colour, the grain is red and the straw has a purple pigment. Under Australian conditions its early growth is prostrate, the plants maturing much later than Federation.

3. EXPERIMENTAL RESULTS.

Bunt.

Segregation in the F_2 Generation.

The percentage of infection obtained in the F_2 generation and parent checks is recorded in Table 1.

TABLE 1.

Bunt Infection in F_2 Generation and Parent Varieties of a Cross Federation × Hope grown at Richmond, N.S.W., in 1931.

Parents of Cross.	Number of Plants.		Percentage of Susceptible Plants.
	Totals.	Susceptible.	
Hope	404	19	4·49
Federation	348	319	91·66
Federation × Hope ..	672	515	76·63

All of the 8 F_1 plants, with the exception of one which was partially infected, were wholly susceptible. In this cross, susceptibility to bunt is dominant to resistance.

The percentage of infection shown by the susceptible parent indicates that only a few plants escaped infection. The resistant parent showed a low percentage of infection. On the assumption of a 3 : 1 expectancy, 504 infected plants would be expected in a population of 672. When the observed numbers are compared by the χ^2 method with the calculated number based on a single factor difference,

$\chi^2=0\cdot960$ and $P=0\cdot36$. This means that, on the basis of random sampling, a deviation as great as, or greater than that observed would be expected 36 times in every 100 trials. The agreement with the expectancy is therefore good.

Segregation in the F_3 Generation.

The F_3 families were inoculated and sown in the same manner as the F_2 generation. The grain was derived from the non-inoculated portion of the F_2 generation sown in 1929. Thus, susceptible families were grown which otherwise would have been lost in the previous generation, as totally smutted plants automatically become eliminated.

Furthermore, individual plants which escape infection, or impurities which become infected, are more easily detected in F_3 rows than as individuals in the F_2 generation.

There were represented 124 F_3 families with check rows of each parent every tenth row. F_3 data are recorded in Table 2.

The average infection of the Hope controls was 4·5 per cent, the spread being over two 10 per cent classes for infection. Of the Federation controls, 92 per cent were infected, ranging from the 81 to 100 per cent class.

The nature of the distribution is seen in Figure 1. Inspection of the line smoothing the curve shows that this

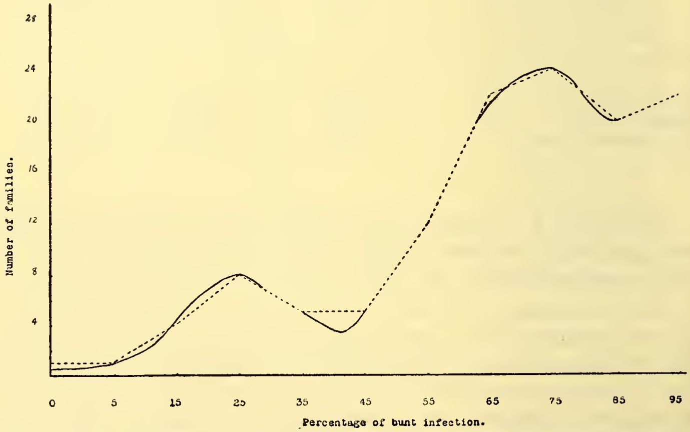

Fig. 1. Distribution of F_3 families of a cross Federation × Hope in 10 per cent classes for bunt infection.

TABLE 2.

Distribution in 10 per cent Classes for Bunt Infection of Parent and F_3 Rows of the Cross Federation × Hope grown at Richmond, N.S.W., 1931.

Parents and Cross.	Distribution of Rows by Percentage Classes for Bunt Infection.											
	0	1 to 10	11 to 20	21 to 30	31 to 40	41 to 50	51 to 60	61 to 70	71 to 80	81 to 90	91 to 100	Number of rows.
Federation	—	—	—	—	—	—	—	—	—	5	10	15
Hope	4	12	1	—	—	—	—	—	—	—	—	17
Federation × Hope	1	1	4	8	5	5	12	22	24	20	22	124

possibly gives a better representation of the curve fitted to the figures in Table 2 than that constructed by joining the points by straight lines. An approximation to a trimodal curve is formed with antimodes at about the 42 per cent and 85 per cent points. Such a curve would suggest the operation of a single factor for resistance to bunt.

In order to satisfy this hypothesis several conditions should be fulfilled. The curves which result from plotting the percentages of infection of the F_3 homozygous families should be similar to those of the homozygous resistant and susceptible parent rows. The hybrid segregates should form a curve about a mean of 75 per cent, which is the average percentage of infection of the F_2 generation. Further, the number of families included under the curves should approximate to a 1 : 2 : 1 ratio.

These conditions are realised in the case of the homozygous susceptible and heterozygous segregates, although somewhat obscured by the overlapping of the two groups. However, although the numbers of homozygous resistant segregates approximate to the expected, they extend over five classes to a minimum at 42 per cent, while the resistant parent rows are dispersed only over three classes.

The sampling errors of the percentage of infection are high due to the comparatively small numbers of plants in the row (about 30 plants). Thus in a single family the addition or subtraction of a plant would be equivalent to a change of 3 per cent on the average, for susceptibility or resistance.

It is possible to consider the graph as a random sample from a variate of positive skewness with no significant variation between the frequencies of the rows with different low percentages of infection. Thus the boundaries of the classes could be selected at any place to the left of 42 per cent or to the right of 85 per cent. Therefore not much faith can be placed in a χ^2 test for comparing the expected frequencies with those obtained in the three classes defined by these two minima.

It appears, then, that the data can be fitted either to a theory of three overlapping distributions or to a single very skew curve. While no definite conclusions can be drawn from the F_3 data alone, they certainly do not contradict the F_2 findings; in fact they probably lend support. The F_2 data give a satisfactory fit to a single factor hypothesis. It is necessary, however, to assume other factors to explain the distribution of the homozygous segregates.

It is suggested that, in addition to a single major factor for resistance to bunt, Hope probably possesses some minor modifying factors which allow the development of bunt in certain families. To test for this possibility all the families in the resistant class were sown, heavily inoculated, in 1932, at the University Farm, St. Paul.

Segregation in the F_4 Generation.

In all, 766 strains representing 27 families from the homozygous resistant group of the F_3 generation were sown together with parent checks. In addition, 89 strains from 22 of these families were sown in four randomised blocks.

Hope, the resistant parent, was entirely free of bunt, and the susceptible parent, Federation, showed only 8·3 per cent infection. Under such conditions the true reaction of the F_4 strains to bunt could not be determined. However, as there were indications that several families were breeding true for a low percentage of infection, seed was selected from 9 of these and sown the following year.

Segregation in the F_5 Generation.

Of the 9 selected F_5 strains which were sown at Richmond, N.S.W., in 1933, six proved to be as resistant as Hope, but three bred true for a low percentage of bunt. Table 3 shows the distribution in infection percentage classes of lines in two of the F_5 strains; Figure 2 graphically represents the same distribution. One strain, selection 19–37–6, is representative of those which bred true for the Hope type of resistance. Selection 89–102–4, with a mean percentage of infection of 17·64±0·0872, is not significantly different from the remaining two, whose means were 18·01±0·7655 and 17·13±0·7887. The mean infection percentage of the parents, Federation and Hope, were 78·66±1·2971 and 2·88±0·6808, respectively.

The fact that selections which breed true for a low percentage of bunt can be made from the resistant group indicates that, in addition to the major factor, there is at least one modifying factor for resistance operating in this cross.

TABLE 3.

Distribution of Parents and Rows in F_5 Strains of the Cross Federation × Hope into 10 per cent Classes of Bunt Infection, grown at Richmond, N.S.W., in 1933.

Parents and Selections.	Distribution of Rows by Percentage Classes for Bunt Infection.									
	0	1 to 10	11 to 20	21 to 30	31 to 40	41 to 50	51 to 60	61 to 70	71 to 80	81 to 90
Federation	—	—	—	—	—	—	—	1	5	3
Hope	2	7	—	—	—	—	—	—	—	—
Selection 19–37–6 ..	8	32	1	—	—	—	—	—	—	—
Selection 89–102–4 ..	—	1	30	10	—	—	—	—	—	—

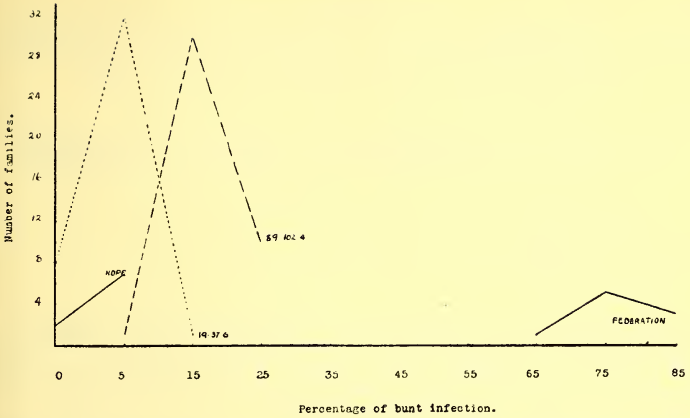

Fig. 2. Distribution of parents and rows in F_5 strains of the cross Federation × Hope in 10 per cent classes for bunt infection.

Stem Rust.

1. Field Results.

F_1 Results. Twenty F_1 plants, sown in the same year as the F_2 and F_3 generations, showed incomplete dominance of susceptibility to stem rust. The only race present was race 34.

F_2 Results. The results of the rust infection in the F_2 generation, consisting of 672 plants, confirmed F_1 evidence, with 42 resistant : 590 intermediate : 40 susceptible plants. The deviation of observed results from an expected 15 : 1 ratio was 2. The $\chi^2{=}0{\cdot}1020$, $P{=}0{\cdot}95$, which closely approximates to a perfect fit.

F_3 Results. Of the 124 families in the F_3 generation, 10 were homozygous for resistance and 7 for susceptibility.

The 107 remaining families showed complex types of segregation which could not be explained on a simple two factor basis. Not only were the reactions of the individuals difficult to classify, but the ratios themselves were not clear cut.

The numbers of each class are shown in Table 4.

If the heterozygotes are grouped and compared with the homozygotes, an approximation to a 1 : 14 : 1 ratio is obtained. $\chi^2{=}0{\cdot}6625$, $P{=}0{\cdot}70$. Alternatively, by grouping the heterozygotes with the homozygous susceptibles a ratio of 114 : 10 is obtained which closely

TABLE 4.

Results of Field Tests for Stem Rust Resistance of F_3 Families of a Cross Federation × Hope grown at Richmond, N.S.W., 1931.

	Homozygous Resistant.	Heterozygous.	Homozygous Susceptible.
Number of families	10	107	7

approximates a 15 : 1 ratio. $\chi^2=0 \cdot 76$ and P=lies between 0·5 and 0·3. Taking into account the F_2 reactions on the population measured with types of F_3 segregations, it would seem that there are at least two factors determining resistance to this form in the field, together with several important modifying factors.

Although various types of resistance to stem rust in the field have been demonstrated, viz. mature plants, functional, morphological and physiological, little, in reality, is known about the factors which control their expression. Some of these factors may operate under one set of conditions and not others, while exactly the reverse may hold for other factors. Thus a considerable variability in the expression of the types of resistance is to be expected as well as several types of segregation.

2. Greenhouse Results.

F_1 Results. Approximately ten seedlings of parent varieties and the F_1 generation were inoculated with race 34 in the greenhouse, with the following results. Federation $\frac{9}{12}$ gave a (4) reaction, Hope $\frac{6}{10}$ a 3-cn reaction, and the F_1 gave $\frac{9}{9}$ seedlings fully susceptible. Unlike the results obtained in the field with the same race, there was complete dominance of susceptibility.

The parent varieties and F_1 seedlings were also inoculated with race 33. Federation was susceptible, Hope resistant and the F_1 resistant. It appears that resistance is dominant when race 33 is used.

F_3 Results. No F_2 seedling tests were made in the greenhouse. The F_3 results were as follows :

TABLE 5.

Results of Testing for Stem Rust Reaction F_3 Seedlings of a Cross Federation × Hope grown in greenhouse at Sydney University and Minnesota, U.S.A., 1933.

Race of Rust.	Number of Families Present in Each Class.					
	Homozygous for Hope Reaction, or Resistance.		Heterozygous.		Homozygous Susceptible.	
	Obs.	Ex.	Obs.	Ex.	Obs.	Ex.
Race 34 ..	28	31	58	62	38	31
Race 33 ..	31	31	58	62	35	31

In both cases a good fit to a 1 : 2 : 1 ratio was obtained, the respective values being for race 33 $\chi^2=0\cdot7741$ and $P=0\cdot68$, and for race 34, $\chi^2=2\cdot1289$ and $P=0\cdot31$.

FLAG SMUT.

Flag smut of wheat, caused by *Urocystis tritici* Koern., is known to occur in China, Japan, India, South Africa, France, Italy, and the United States of America. It was first officially recorded in Australia in 1868 by the South Australian Commission on Cereal Diseases,(58) and since that time has spread through most of the wheat-growing areas, becoming one of our worst cereal diseases. Fields showing as much as 90 per cent infection and 50 per cent loss have been recorded. The annual loss due to this smut alone has been estimated at £400,000.(23) Noble(56) estimated an annual loss of 2,000,000 bushels.

While most of the varieties grown commercially in Australia are susceptible to *Urocystis tritici*, some are notably resistant. In 1932 Nabawa was the most popular wheat grown in Western Australia, South Australia, and New South Wales—this popularity being due mostly to its flag smut resistance. However, even though a plant may not show the typical symptoms of the disease, loss in yield may accrue due to " suppressed " infection.(52)

While considerable work has been done in synthesising such resistant varieties, little is known about the mode of inheritance of resistance.

Verwoerd(71) found in crosses between resistant and susceptible parents that resistance was inherited along Mendelian lines but could not determine the number of factors operating.

In the present study only the F_3 families of a cross Federation (susceptible) × Hope (resistant) were tested for their reaction to flag smut.

The percentage of infected plants per family was calculated and the families were placed in 10 per cent classes for infection. The distribution is set out in Table 6.

The average infection of the Hope controls was 4·2 per cent, the spread being over two classes. There were 65·7 per cent, on the average, of the Federation controls infected; they ranged from the 50 to 90 per cent class.

The nature of the distribution is seen in Figure 3.

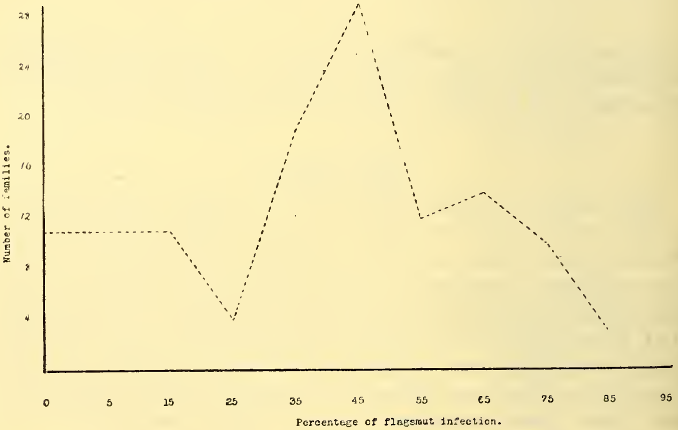

Fig. 3. Distribution of F_3 families of the cross Federation × Hope in 10 per cent classes for flag smut infection.

A trimodal curve, indicating a 1 : 2 : 1 ratio is seen. The first minimum lies at 25 per cent and the second one at 55 per cent. These two minima do not strictly divide the phenotypes; there is a certain amount of overlapping at these points.

Table 6.

Distribution in 10 per cent Classes for Flag Smut Infection of the Parent and the F_3 Rows of a Cross Federation × Hope grown in greenhouse at St. Paul, Minnesota, U.S.A., in 1932.

Parents and Cross.	Distribution of Rows by Percentage Classes of Flag Smut Infection.											
	0	1 to 10	11 to 20	21 to 30	31 to 40	41 to 50	51 to 60	61 to 70	71 to 80	81 to 90	91 to 100	Number of Rows.
Federation	—	—	—	—	—	—	7	8	8	6	—	29
Hope	12	13	2	—	—	—	—	—	—	—	—	27
Federation × Hope	11	11	11	4	19	29	12	14	10	3	—	124

In the absence of F_1 and F_2 data, fuller details in the mode of inheritance are lacking. The F_3 results, however, would seem to indicate the action of a single major for resistance. Modifying factors may also be present, but no attempt was made to identify any of these. The detection of infected plants which do not have typical disease symptoms presents difficulties in classification. This condition is usually manifested by distinct stunting in plant growth (Plate XII). A histological examination of the leaves of such plants showed that typical smut mycelium was present in the host tissues.

AWNEDNESS.

Biffen(5) was one of the earliest workers to study the inheritance of awnedness and found the beardless condition in wheat to be dominant. Stewart and Tingey(69) explain the breeding behaviour of a wheat cross, Marquis × Federation, by a single factor difference. Gaines and Singleton(31) found a ratio of 3 awnless : 1 awned in the F_3 generation of a cross Turkey × Marquis. In a cross between a ful.-awned variety, Utac × Ridit, which is short apically awned, Stewart and Dalley(66) found 1 : 2 : 1 ratios. The writer(15) obtained similar results in studying the inheritance of tip beard in a Florence × Hard Federation cross. There appears to have been some confusion in the use of the terms awnless and awned, the latter being used by some of the authors to designate the tip-awned condition which is class 3 in this study.

Howard and Howard(49) were the first to work with fully awned and awnless wheats and recorded two factors for the inheritance of this character, with dominance of awnedness. This conclusion was evidently based on the comparison of all awned and tip-awned classes, which gave a ratio of 15 : 1.

Clark,(18) however, concluded that awnlessness was dominant in a cross Kota × Hard Federation because the F_1 more closely approached the awnless (Hard Federation) than the awned parent (Kota). He could not satisfactorily explain the breeding behaviour of the F_2 and F_3 generations on a two factor basis.

Clark and Hooker,(21) Stewart and Heywood,(67) Stewart and Judd,(68) and Clark, Quisenberry, and Powers(22) have explained the inheritance of beard on a two factor basis.

Ratios of 9 awned : 7 awnless plants were found in F_2 generations by Regot(60) in crosses between these types of wheats. He postulates the existence of two factors, one of which must be present in the homozygous condition for the development of awns.

Clark, Florell and Hooker(20) classified the hybrids of a wheat cross into five classes: (i) awnless, (ii) apically awnletted, (iii) awnletted, (iv) short awned, (v) awned.

The genetic interpretation of a Bobs × Propo cross was made on the basis of two major factor pairs (AA and BB) and for Bobs × Hard Federation two minor factor (CC and DD) pairs. Two major and one minor pairs were necessary to explain the genetic behaviour in the Federation × Propo cross. The effect of the minor factors in the presence of the major factors was to reduce the extent of awnedness. He concludes that there are as many as four genetic factors involved in the inheritance of awnedness.

In the present study the two parents, Federation and Hope belong respectively to classes 1 and 5. The segregating families in the F_2 and F_3 generation were separated into classes suggested by Clark, Florell and Hooker(20) and are illustrated in Plate XIII.

F_1 Results. The F_1 plants were intermediate for awnedness but more like Federation than Hope. This indicates incomplete dominance for awnlessness.

F_2 Results. The segregation in the F_2 generation is set out in Table 7.

TABLE 7.

Segregation for Awnedness in F_2 Generation of a Cross Federation × Hope grown at Richmond, N.S.W., in 1931.

Class.	Number of F_2 Plants.	
	Obs.	Ex.
(1) Awnless	59	47
(2) Apically awnletted	345	336
(3) Awnletted..	142	168
(4) Short awned	85	84
(5) Awned	41	42

On the basis used for classification, the ratio approximates to 1 : 8 : 4 : 2 : 1. The χ^2 for goodness of fit to this ratio is 4·3, with a P value of 0·37.

There appears to be two factors for awnedness operating in this cross.

F_3 Results. Using the same basis for classification, 124 families were classified by their F_3 breeding behaviour. The results are as follows :

TABLE 8.

Breeding Behaviour in respect to Awnedness of F_3 Families of a Cross Federation × Hope grown at Richmond, N.S.W., 1931.

Class.	Number of Families.	
	Obs.	Ex.
(1) Breeding true for class 1 ..	5	7·75
(2) Segregating for classes 1, 2 and 3, or 1, 2, 3, 4 and 5	67	62·0
(3) Breeding true or segregating for classes 3 and 5	27	31·0
(4) Segregating for classes 3, 4, 5 ..	21	15·5
(5) Breeding true for class 5 ..	4	7·75

The χ^2 for goodness of fit for a 1 : 8 : 4 : 2 : 1 ratio = 7·7901, and the P value = 0·09.

The fit is significant but a poor one. It should be remembered that there is much overlapping of the classes and the separation of the types is often difficult. Thus, long awnlets at the tip of the ear could be mistaken for short awns.

Among the F_3 progeny were noticed two new types which bred true. One type had full awns at the tip with entire absence of awns or awnlets on the lateral spikelets, while the other had long awnlets on all spikelets without any awns at the tip. This would seem to indicate the independent operation of factors for awnedness on different parts of the wheat head.

The difficulties in classification and interpretation of results are discussed elsewhere (p. 580).

GROWTH HABIT.

Wheats have been described (Clark *et al.*(22)) as having winter growth or spring growth habit.

In their early growth the winter wheats are prostrate, whereas spring wheats are erect, although in some cases winter wheats may have erect growth in the fall. Some varieties are somewhat intermediate or facultative in their growth habit; Hope may be sown in the spring or fall.

In Australia most of the varieties have spring growth habit, and although sown in late autumn or fall, owing to the mild nature of the winter, they maintain their erect habit. Even under these conditions, however, Hope remains prostrate for some time (Plate XII, below).

Several investigators have studied the behaviour of the segregating hybrids of crosses between spring and winter wheats. The results, however, owing to the strong influence of environmental conditions, are generally not conclusive and sometimes even contradictory.

Spillman(62) states that winter growth habit is dominant over spring growth habit, while dominance of spring growth habit is claimed by other workers (Aamodt,(1) Gaines and Singleton,(31) Vavilov, N. I. and C. S. Kouznetsov (see (59)).)

Aamodt(2) obtained a ratio of 15 spring to 1 winter in the F_2 of crosses between Marquis, Kota and Kanred.

In crosses between several spring and winter wheats, Cooper obtained ratios of 13 spring forms to 3 winter, where Marquis was used as the spring growth habit parent, and 3 spring : 1 winter, when Haynes Bluestem was used. He explained his results by assuming the action of an inhibitor on factors for spring growth habit.

Quisenberry(59) studied the inheritance of growth habit in crosses between Minhardi winter and H44 spring wheats and found dominance of spring habit. Limited F_2 data indicated a ratio of 15 having spring growth : 1 having winter growth habit. A genetic explanation of growth habit, segregation in F_3, is suggested by assuming two dominant duplicate factors for spring growth habit.

In the present study, the early prostrate growth of Hope, compared with the erect growth of Federation, is the character under consideration. Hope heads out normally about 14 days later than Federation, although maintaining the prostrate habit for approximately four months after germination.

The F_1 plants were rather intermediate in character but more like the Federation parent, indicating an incomplete dominance of spring wheat habit.

F_2 Results. The F_2 plants were divided into three groups: (i) spring, (ii) intermediate, and (iii) prostrate habit. The numbers in each class were: class (i), 181; class (ii),

319; class (iii), 172. This approximates a 1 : 2 : 1 ratio, χ^2 for goodness of fit being 1·9612 and P=0·38. The results indicate that a single factor determines the inheritance of spring habit.

F_3 Results. In the F_3 families there were 25 homozygous for spring growth habit, 75 heterozygous and 24 homozygous for winter habit. This gives a fair approximation to a 1 : 2 : 1 ratio giving a χ^2 for goodness of fit 5·4, P=0·07. The results indicate the dominant reaction of a single factor, but probably several others are also operating.

EMERGENCE OF LEAF FROM COLEOPTILE.

It is known that many smuts gain entrance to their hosts by penetration of coleoptile. Knowledge of conditions of plant growth from the time of germination until the first leaf breaks through the coleoptile is important, therefore, in the study of resistance to such smuts.

The F_3 families grown in the greenhouse in the rust and flag smut trials were examined and notes were taken on the date of emergence of the first leaf. Under the prevailing experimental conditions the first leaf of Federation emerged four days before that of Hope.

The plants were divided into three classes:

(1) with first leaf appearing as soon as Federation controls,
(2) intermediate,
(3) with first leaf appearing as late as Hope controls.

The F_3 families were classified as homozygous or heterozygous. The results are presented in Table 9.

TABLE 9.

Breeding Behaviour with respect to Appearance of First Leaf of F_3 Classes of a Cross Federation × Hope grown in greenhouse Minnesota, U.S.A., 1933.

Class.	Number of F_3 Families.	
	Obs.	Ex.
1	25	31
2	72	62
3	27	31

The χ^2 for goodness of fit to a 1 : 2 : 1 ratio is 3·2902 $P=0\cdot19$, indicating a fair fit.

It appears that a single factor determines the speed of emergence of the first green leaf from the coleoptile in this cross.

MATURITY.

Early maturing varieties of wheats, whose precocity is the means of escaping unfavourable conditions induced by climate or crop pests, are desirable in most wheat-growing areas.

William Farrer(24) observed that the F_1 of a cross was intermediate between the parents in time of ripening. Biffen(5) crossed an early (Polish) and a late (Rivet) wheat, and found the F_1 to be almost as late as the Rivet wheat. Similar results were obtained by Thompson,(70) who found in a number of crosses that the ripening period of the F_1 was near the mean of the late parent. He found also that the F_2 individuals varied in range from almost the early to the late parent.

Freeman(29) found the average date of heading of the first F_2 and F_3 progenies were intermediate or nearer to that of the late parent.

Florell(28) on the other hand, in a wheat cross, Sunset (very early) and Marquis (midseason to late in California) found two distinct heapings into a larger early group and a smaller late group approximating at 3 : 1 ratio. He explained the segregation of families in another cross by two or three factors.

Clark(18) in a Kota × Hard Federation wheat cross found that earliness was dominant to lateness. Clark and Hooker(21) found in the F_2 of a Marquis × Hard Federation cross that early heading was partially dominant.

In the present investigation, the appearance of the tip of the first spike of the plant was taken as an index of earliness for it was considered that this period is less affected by environmental conditions than at any time in ripening. Moreover there is a close relation between the various stages of ripening from the peeping ear to the fully ripe grain.(28)

F_1 Results. The F_1 plants in this cross were intermediate in earliness between the two parents, with mean closer to that of the earlier parent. The mean number of days from sowing until ear-peeping stage for the Hope and

TABLE 10.

Distribution of F_2 Plants in One-day Classes for Appearance of First Head in a Cross Federation × Hope Grown at Richmond, N.S.W., in 1931.

—	Number of Days from Sowing to Appearance of First Spike.																		
Parents and cross ..	118	119	120	121	122	123	124	125	126	127	128	129	130	131	132	133	134	135	136
Federation	49	104	98	7	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Hope	—	—	—	—	—	—	—	—	—	—	—	—	2	20	52	88	107	32	20
F_2	46	60	125	111	69	59	16	14	14	11	10	10	6	15	42	40	14	10	—
	231			320										121					

Federation wheats respectively were 133 and 119 days, while that of the F_1 plants was 124 days.

F_2 Results. The F_2 data with dates of appearance of first ear of parent varieties are recorded in Table 10. The data show large early and smaller late groups. None of the (42) families were later or earlier than their respective parents.

It is interesting to note that practically all of the plants of the Federation parent showed the first spike within three days. There appears to be dominance of earliness.

Attempts to analyse the F_2 data on a factorial basis have failed. There appears to be a number of factors which determine maturity in this cross.

F_3 Results. The F_3 families were divided into five groups according to the range of dates of ear peeping. Thus families in which all plants showed the ear peeping before 121 days were placed in one group. In others, this stage extended up till the 130th day and therefore included F_2 classes 1 and 2, and so on. The results are as follows :

TABLE 11.

Breeding Behaviour in Relation to Earliness of F_3 Families of a Cross Federation × Hope grown at Richmond, N.S.W., in 1931.

F_3 Groups.	Range of Earliness according to F_2 Classes.	Numbers of Families.
	Class.	
1	1	28
2	1 and 2	28
3	1, 2 and 3	46
4	2 and 3	11
5	3	11

The data as arranged do not admit of analysis on a factorial basis. The small number of the double recessive class (5) would suggest that more than one factor is operating.

COLEOPTILE COLOUR.

The coleoptile, the sheath covering the first foliage leaf of the wheat plant as it emerges from the soil, may be colourless, pale green, or pink.(57)

The coleoptiles of Hope have a distinct purple colour which may persist for some time after the first leaf emerges. The coleoptiles of Federation are colourless.

The development of the colour varies with changing environmental conditions, but under the experimental greenhouse conditions little variation was noticed between the different sets. Notes were taken on the colour of the coleoptile of emerging seedlings used in the rust and flag smut tests. In this way four replications of each family were available. No attempt was made to separate out the intermediate shades of purple, all coloured coleoptiles being grouped as purple.

Goulden, Neatby and Welsh(36) postulate a two-factor basis of the inheritance of this character in a cross, H44–24 × Marquis. A two-factor hypothesis is advanced to explain the segregation used in a Minhardi × H44 cross.(59) Recently, however, Ausmeus(4) found a single factor difference for colour between Hope and Marquillo or Supreme.

F_3 Results. No notes were taken in the F_1 and F_2 generations. The ratios of the families breeding true for purple colour, segregating and breeding true for lack of colour was 10 : 104 : 10. Superficially, this would suggest that two factors are responsible for the purple coleoptile pigment in Hope.

However, amongst the F_3 heterozygous families, the segregation for white and purple colour was most confusing. The separation of the colour types proved most difficult, and it is doubtful whether the inheritance could be explained on a simple two-factor basis.

The number in each class are set out in Table 12.

TABLE 12.

Distribution of F_3 Families Segregating for Coleoptile Colour in Federation × Hope Cross grown in greenhouse, Minnesota, U.S.A., 1933.

	Purple.	Segregating.	White.
Number of families	10	104	10

These members approximate to a 1 : 14 : 1 ratio. $\chi^2 = 1 \cdot 3270$ $P = 0 \cdot 50$.

If the homozygous purple and segregating families are grouped and compared with the colourless a ratio of 114 : 10 is obtained, which approximates to a 15 : 1 ratio. $\chi^2=0 \cdot 6967$, $P=0 \cdot 41$.

It would seem that there are at least two factors present in Hope determining purple pigmentation of the coleoptile.

STALK COLOUR.

Purple pigment is found in the straw of a number of well known varieties. It is present in Hope but absent in Federation. In the F_2 generation plants were separated into two bundles—pigmented and unpigmented—and a ratio of 556 purple : 106 white was obtained, which does not indicate the number of factors operating.

As was the case with coleoptile colour, while no difficulty was experienced in separating the homozygous classes, the heterozygous types were hard to classify.

By grouping the individuals in a manner somewhat similar to that observed for coleoptile colour, results were obtained which are recorded in Table 13.

TABLE 13.

Distribution of F_3 Families Segregating for Stalk Colour in a Cross Federation × Hope grown at Richmond, N.S.W., in 1931.

	Homo-purple.	Segregating.	Homo-white.
Number of families	8	106	10

This approximates to a 1 : 14 : 1 ratio. $\chi^2=0 \cdot 5069$, $P=$approx. $0 \cdot 80$.

If the first two classes are combined, a ratio of 114 : 10 is obtained. $\chi^2=0 \cdot 6967$, $P=0 \cdot 41$.

At least two factors determine stalk colour in this cross.

GRAIN COLOUR.

Biffen⁽⁵⁾ was the first to report the dominance of red colour over white in wheat cross, which segregated in a 3 : 1 ratio in the F_2 generation. Nilsson-Ehle⁽⁵⁵⁾ later found F_2 generations of certain crosses giving 15 : 1 and 63 : 1 ratios, indicating the presence of two and three factors. Since then other workers have found similar ratios.

In the present cross red proved dominant in the F_1, and no white grain was found in the F_2.

The grain of the F_3 families was divided into five classes according to the degree of redness. The classes were as follows: (1) white, (2) near white, (3) intermediate, (4) near red, (5) red. Some of the families were homozygous for white colour, some for red, whilst the remainder segregated. For sake of simplicity the F_3 families are classified, on the basis of their segregation, as the F_2 phenotypes from which they are derived. The classification is as follows:

(1) White	3
(2) Near white	18
(3) Intermediate	74
(4) Near red	26
(5) Red	3

There are 121 red families to 3 white. The expected ratio on a three-factor basis with this population is 122 : 2 (approx.) and the $\chi^2 = 0\cdot5918$, $P = 0\cdot45$. There appear to be three factors responsible for red kernel colour in Hope, which are lacking in Federation.

INTERRELATIONS OF HERITABLE CHARACTERS.

From the plant breeder's point of view alone it is important to know if any linkage exists between the genes for resistance to disease and genes for other physiologic and morphologic characters.

In 1919 Fischer(26) noted an association between resistance to *Gymnosporangium juniperum* and the leaf shape of the F_2 progeny of a cross between two species of *Sorbus*; susceptibility was linked with bipinnate leaves.

Rieman(61) found a close relationship between pigmentation in the onion and resistance to *Colletotrichum circinans*.

In the cereals, linkages between genes for seed colour and those modifying resistance to a mixture of the smuts of oats were postulated by Garber *et al.*(33) Griffee(38) believed that the three genes for resistance to *Helminthosporium sativum* in barley were respectively linked with those for glume colour, ear shape, and smooth condition of the awns. Clark(18) found a correlation between time of heading out and resistance to stem rust.

Few cases are known of linkage existing between genes for resistance to the various diseases. According to Hayes, Aamodt, and Stevenson(45) the genes for resistance to *Puccinia triticina* and *P. graminis tritici* are linked. Similar results were obtained by Hayes *et al.*,(46) Stevenson,(65) and Waterhouse,(72) who also demonstrated linkage between resistance to leaf rust and resistance to powdery mildew.

In 1929 Goulden and Neatby(35) found a genetic linkage, which was not definite, between field resistance to *P. graminis tritici* and susceptibility to black chaff, caused by *Bacterium translucens* var. *undulosum* in a variety H44–24. Recently Ausmeus(4) has reported a tendency towards linkage between field resistance to *P. graminis tritici* race 36, and susceptibility to black chaff in several Hope crosses.

In the present study all the possible comparisons were made between resistance to certain diseases and other physiological and morphological characters. The results are recorded in Tables 14, 15 and 16, which set out the independent inheritance of, (*a*) reactions to various disease resistant characters, (*b*) disease and other physiologic and morphologic characters, and (*c*) morphologic characters.

Fisher(27) draws attention to the fact, that, since the calculated distribution of χ^2 is not realised in small classes, it is not wise to set up a contingency table where many of the classes have expectancies of less than five. The population of 124 in the present study was small enough to give, in 7×7, 7×5, and 5×5 tables, expected class numbers less than five fairly frequently. When this occurred the classes of low expected frequency were grouped. Cases where groupings could not be made to ensure a valid χ^2 are not included in the tables.

TABLE 14.

Independent Inheritance of Characters in the F_3 Generations of a Cross Federation × Hope.

Characters Compared.	n	χ^2	P
Stem rust, race 34 (field) and stem rust race 33	8	9·93	0·27
Stem rust, race 34 (field) and stem rust, race 34 (greenhouse)	8	7·34	0·50
Stem rust, race 34 (field) and bunt ..	8	21·33	<0·01
Stem rust, race 34 (field) and flag smut	8	25·83	<0·01
Stem rust, race 34 (greenhouse) and stem rust race 33	4	14·38	<0·01
Stem rust, race 34 (greenhouse) and bunt	4	1·11	0·90
Stem rust, race 34 (greenhouse) and flag smut	4	7·37	0·12
Stem rust, race 33 and bunt	4	2·58	0·64
Stem rust, race 33 and flag smut ..	4	6·27	0·18
Bunt and flag smut	4	19·06	<0·01

TABLE 15.

Independent Inheritance of Characters in the F_3 Generation of a Cross Federation × Hope.

Characters Compared.	n	χ^2	P
Stem rust, race 34 (field), and habit ..	8	8·40	0·39
Stem rust, race 34 (field), and maturity	8	50·49	<0·01
Stem rust, race 34 (field), and leaf emergence	8	8·70	0·37
Stem rust, race 34 (greenhouse), and awnedness	8	5·07	0·76
Stem rust, race 34 (greenhouse), and grain colour	8	2·98	0·94
Stem rust, race 34 (greenhouse), and habit	4	7·57	0·11
Stem rust, race 34 (greenhouse), and maturity	8	3·36	0·91
Stem rust, race 34 (greenhouse), and leaf emergence	4	1·10	0·89
Stem rust, race 33, and awnedness ..	8	9·15	0·33
Stem rust, race 33, and grain colour ..	8	7·40	0·49
Stem rust, race 33, and habit	4	1·72	0·79
Stem rust, race 33, and maturity ..	8	14·29	0·06
Stem rust, race 33, and leaf emergence	4	8·53	0·07
Bunt and awnedness	8	9·43	0·31
Bunt and grain colour	8	6·73	0·56
Bunt and habit	4	14·65	<0·01
Bunt and maturity	8	15·99	0·05
Bunt and leaf emergence	4	2·25	0·69
Flag smut and awnedness	8	4·03	0·83
Flag smut and grain colour	8	8·33	0·40
Flag smut and habit	4	5·02	0·29
Flag smut and maturity	8	10·87	0·21
Flag smut and leaf emergence ..	4	5·43	0·25

TABLE 16.

Independent Inheritance of Characters in the F_3 Generation of a Cross Federation × Hope.

Characters Compared.	n	χ^2	P
Awnedness and habit	8	5·18	0·74
Awnedness and leaf emergence ..	8	4·74	0·78
Grain colour and habit	8	12·79	0·12
Grain colour and leaf emergence ..	8	6·14	0·62
Stalk colour and coleoptile colour ..	8	350·49	0·01
Habit and maturity	8	9·09	0·33
Habit and leaf emergence	4	4·17	0·38
Maturity and leaf emergence	8	7·73	0·46

The comparisons indicate that most of the characters which were studied were independently inherited. There is a strong linkage between the genes determining coleoptile and stalk colour. The formula $\sqrt{2\chi^2}-\sqrt{2n-1}$ was used in this for a normal deviate with a unit standard error. The value of 36·02 which was obtained indicates very significant linkage. There appears to be a loose association between the inheritance of resistance to race 34 of stem rust in the field and late maturity, and also between resistance to bunt and flag smut. Doubtful or very weak linkage is indicated between the genes determining resistance to bunt and Hope habit of growth and also resistance, in the greenhouse, between races 33 and 34 of stem rust.

DISCUSSION.

A feature of recent advances in plant pathology and plant genetics is an appreciation of the complicated and interdependent nature of the factors which influence and condition the various phenomena studied in these sciences. This is reflected in the definite attempts of investigators to measure the relative effects of a number of variables which collectively bring about a certain reaction, and is probably the logical outcome of a growing refinement in technique. While many investigators in the past, from studies on the nature and inheritance of disease resistance have explained genetical happenings by the action of one, or at the most, very few factors, more recently it has been realised that modifying factors frequently play an important part.

Inheritance of Resistance to Bunt.

In studies dealing with bunt, Gaines,(30) from his earlier work, postulated several genes for resistance to bunt in varieties of wheat. These conclusions are not surprising when it is remembered that his inoculum may have been a mixture of physiologic races. At that time, he believed that *Tilletia spp*. comprised a single race. In the light of recent work on physiologic specialisation in bunt, it is highly probable that his inoculum contained a mixture of races. In his later work,(32) he obtained simple mono- and di-hybrid ratios, when a single race was used. However, his original multiple factor hypothesis is supported by other workers as Aamodt,(3) Clark, Quisenberry, and Powers,(22) and Kilduff.(50)

On the other hand Briggs,(14) using one physiologic race, has demonstrated single factor differences between a number of varieties. Hussar possesses two factors. In all, he has demonstrated three major factors which have been designated as the Martin, Hussar, and Turkey factors and, in addition, several modifiers. He gives the genotypes of several varieties in respect of bunt resistance as follows :

Martin		MM	h h	t t
Hussar		MM	HH	t t
Selection	1418	mm	HH	t t
Turkey	1558	mm	h h	TT

The recessive factor possessed by Florence, which was demonstrated by the writer,(16) is the fourth known factor. There are 16 different homozygous combinations possible between these genes. It is probable that as the work on the genetics of bunt resistance progresses, new factors will be determined with accompanying complication of the mode of inheritance.

The truth regarding the nature of the inheritance of resistance to bunt seems to lie between the multiple factor hypothesis postulated by Gaines and that of single factors maintained by Briggs. Probably one or two major factors determine resistance, with one or more minor factors acting as modifiers. Results in the present work support this contention. In a wheat cross Federation × Hope, there is a single major factor difference for resistance, but in addition there is at least one modifying factor which allows the production of a low percentage of bunt in certain resistant families.

Adoption of Criteria.

The interpretation of any genetical analysis depends largely upon the criteria adopted for classifying the variants. Hansen(50) has pointed out that, while the resistance of an individual plant to rust or mildew can fairly easily be determined in F_1 and F_2 generations, this is much more difficult to do with the smut fungi. Here the degree of infection is expressed as the percentage of susceptible individuals in a F_3 family. Theoretically, the method would allow of a phenotypic classification of individuals in the F_2 generation given a 100 per cent infection of the susceptible and 0 per cent in the resistant parents. However, this condition is seldom, if ever, realised, owing to several reasons of which disease escape is the most important. Hence a simple segregation is often masked.

Most workers divide the F_3 bunted families into classes of equal magnitude according to infection percentages and construct a curve from these figures. The class limits of the genotypes are placed at the minimal points of the curve. At present this appears to be the only satisfactory practical method of classifying F_3 families for reaction to bunt or flag smut. Even this method, in which evident sporulation is adopted as the criterion for susceptibility, has obvious weaknesses. Under certain conditions, some plants of the resistant parent show a " late-tiller " infection. Only the late lower shoots, which normally do not produce ears, are infected, and yet the yield of the plant is apparently unaffected. In the present study such plants are deemed resistant.

Again, it is known that the fungus causing flag smut in wheat may be present in host tissues without ever becoming apparent. Such plants are stunted in growth and invariably have a " sick " appearance (Plate XII, upper). Stained sections through the leaves show the presence of smut mycelium, usually adjacent to the vascular system. This type of infection, which has lately been referred to as " suppressed infection," undoubtedly causes heavy losses in yield.(52) Yet, for purposes of genetical classification such plants are resistant.

The difficulties in classifying the disease reaction of plants will be overcome only when the nature of resistance to disease has been determined and in the light of this knowledge, criteria for susceptibility have been set up and universally adopted. It has been shown that, under certain conditions, the mycelium of germinating flag smut spores enters and becomes established in the young tissues of developing wheat seedlings of *monococcum*, *dicoccum*, and *vulgare* types. At present it is not known what prevents further development in resistant varieties. The optimum conditions for the production of the flag smut infection in the present studies was obtained by pre-soaking inoculum and grain, and holding the germinating wheat seed at a temperature of 21° C. The spores were pre-soaked in tap water for 48–60 hours and the grain was added to this suspension 8–12 hours before sowing. Further details are recorded elsewhere.(17)

It has been pointed out in an earlier part of this paper that the method for determining the percentage of bunt in the row was similar to that adopted by Briggs, viz., a percentage of infected plants. His objection to Gaines' method on the grounds that a plant loses its genetic identity seems reasonable. However, Harrington[2] and Clark *et al.*(22) have shown a high correlation between the percentage of infected plants and the percentage of infected heads in the row. The positive correlation of $r = 0 \cdot 741 \pm 0 \cdot 029$ is important from a plant breeding standpoint, allowing selections to be made by a head count in the row. Nevertheless it is considered advisable, in genetic studies, to maintain Briggs' method for estimating the infection percentage.

There is a certain danger in arbitrarily fixing artificial limits between susceptible and resistant F_3 families, for as Hansen(39) states, "workers may start from what has to be proved: an explanation according to Mendelian laws is admitted *a priori*, and the results are adjusted accordingly". The greatest care then should be exercised in setting up the limits of reaction and in adopting criteria for susceptibility and resistance.

Importance of Environmental Factors.

The position is further complicated by the environmental factor. It is not surprising to find that an individual plant may vary in resistance at different ages and under changing environmental conditions. Furthermore the different types of resistance depend on separate genes. Hayes *et al.*,(48) working with certain forms of stem rust, have shown that field resistance was inherited quite independently of "greenhouse" resistant seedlings. In the progeny of a cross, in which Marquillo was a parent, they obtained mono-hybrid ratios in the greenhouse and di-hybrid segregation in the field. Other workers(34, 36, 53, 59) have demonstrated how different factors for resistance may operate at different ages in the life of a plant. The present study confirms these results. It is interesting to note that from the cross Federation × Hope every seedling selected in the greenhouse for the Hope or 3-cn reaction to race 34 showed mature plant resistance when planted in the field.

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[2] Unpublished data kindly supplied by Dr. J. B. Harrington in 1932.

Waterhouse[3] states that an examination of F_3 families of the cross Federation × Hope for reaction to stem rust race 34, at a certain time during the growing season gave clear indication of the operation of a single factor for resistance. A later examination of the same material gave ratios indicating the action of two factors. Only race 34 was present. It appears that the operation of a gene is dependent on certain environmental conditions, and unless these are attained its action does not become evident.

This is probably true also with the smuts, although such a condition has not been demonstrated. The low percentage of infection obtained in the susceptible parent and F_4 families when sown at Minnesota, U.S.A., in 1932 is worthy of consideration. As far as could be determined, the inoculum comprised a single race and was obtained from the heads of susceptible plants which, in the previous year, had given 92 per cent infection. That the inoculum was viable is shown by the infection of Progress and Kota (60 per cent) when grown under the same conditions. It is possible that, under a different set of environmental conditions to those prevailing in Minnesota, the full expression of the genes' activities may have been attained. By the same token, the infection of Kota, which is adapted to growing in these regions, was to be expected.

This paper deals chiefly with the genetics of disease resistance but also includes morphological studies. A critical examination of the inheritance of certain morphologic characters, which in themselves presented complicated problems, has not been attempted. Thus no adequate explanation is given for the mode of inheritance of maturity. There are certainly several factors which appear to come into operation at different times, and it is considered that environmental conditions must play an important part in their activation.

Growth habit and time of emergence of first leaf appear to show single factor differences. Two factors are operating for coleoptile and stalk colour, while three determine the mode of inheritance of grain colour. In each case environment is important in the expression of the character. Thus the degree of purpleness in the coleoptile varies greatly with the light intensity.

The environmental factor is particularly important in the expression of the degree of awnedness. An examination

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[3] Unpublished data kindly supplied by Dr. W. L. Waterhouse in 1934.

of Plate XIII, lower) will show the variation in the length of awn on heads of homozygous full-bearded heads, when grown in different years, one being the progeny of the other. Since the present classification is essentially one of measurement, its unsatisfactory nature is illustrated by the variation in length of awn which may occur in different years. For example, distinct differences are noticeable in Federation. When grown under Australian conditions it is classified as bald, but it develops an appreciable tip awn when grown under certain field conditions in U.S.A. Hence, the classification of awnedness which normally is difficult on account of overlapping class may become very complicated.

An attempt was made to classify the families of the cross studied on a different basis to that suggested by Clark. Some families bred true for awn at the tip only ; others for lateral awns. The families were grouped into expected classes, assuming the operation of two factors, one for the production of lateral awns, the other for tip awns. There are indications that the assumption may be true, but, in the absence of confirmatory evidence, the data are not presented. Further studies utilising back cross and advanced generation material are planned to test the validity of the supposition.

Conclusion.

Considerable stress has been laid on the importance of the effects of environmental factors in pathologic and genetic studies. It is necessary to do this, for, very often, investigators, in dealing with inherent qualities of the plant, lose sight of the significance of external factors. Disregard of the need of definition or attempted standardisation of experimental conditions has made a comparison of valuable results impossible. Clearly there is an urgent need for the adoption of standardised technique, which embraces an agreement concerning the criteria to be used and the general environmental conditions under which the investigations are to be carried out.

SUMMARY.

1. In a wheat cross, Federation × Hope, studies were made at Richmond, New South Wales, Australia, and University Farm, St. Paul, Minnesota, U.S.A., in the greenhouse and in the field, on the inheritance of resistance

to bunt, to flag smut, to two races of stem rust, and of certain morphological characters. The interrelations of the inheritance of all the characters in the cross were also studied.

2. Field results extending over five generations and using a single collection of *T. tritici* indicate that, in addition to a single factor for resistance, there are one or more modifiers acting in this cross, which allows the development of a small quantity of bunt in resistant lines.

3. Resistance to stem rust, race 34, in the field is determined by at least two factors and probably several other important modifying factors. Single factors, which are inherited independently of those for resistance in the field, determine resistance to races 33 and 34 in the greenhouse.

4. The reactions of F_3 lines in the greenhouse to *Urocystis tritici*, which causes flag smut of wheat, indicate the operation of a single major factor for resistance. Hope is resistant. In the absence of F_1 data the dominant reaction is not known.

5. In this cross the varieties show a single factor difference for growth habit and time of emergence of the first leaf. Two factors are operating for coleoptile and stalk colour and expression of awnedness, while three determine the mode of inheritance of grain colour. The mode of inheritance of maturity is not satisfactorily explained ; there appear to be several factors acting which come into operation at different times.

6. Studies on the interrelations of the heritable characters show a strong linkage of genes which determine stalk and coleoptile colour. There are also indications of loose linkage between genes for resistance to bunt and flag smut, resistance to race 34 of stem rust in the field and maturity, and resistance in the greenhouse to races 33 and 34 of stem rust.

7. The present position regarding the genetics of bunt is discussed and observations are made on the adoption of criteria in studies in plant genetics, the importance of the environmental factors and the need for the standardisation of conditions under which investigations are carried out.

EXPLANATION OF PLATES.

PLATE XII.

Above.—Stunting produced by *Urocystis tritici* in wheat plants grown in greenhouse, St. Paul, Minnesota, U.S.A., 1932. Federation plants, A not infected, B infected.

Below.—Growth habit of the parents and F_3 rows of a cross Federation × Hope. Row A, Federation ; Row B, Hope ; Rows C and D, segregating F_3 rows.

PLATE XIII.

Above.—Wheat heads of a homozygous full-awned Class (5), grown in different years at Richmond, New South Wales.

A, grown in 1931 ; B, progeny of A, grown in 1933.

Below.—Awned classes, according to Clark, found in the segregating generations of a wheat cross Federation × Hope.

1, Awnless ; 2. apically awnletted ; 3, awnletted ; 4, short-awned ; 5, awned.

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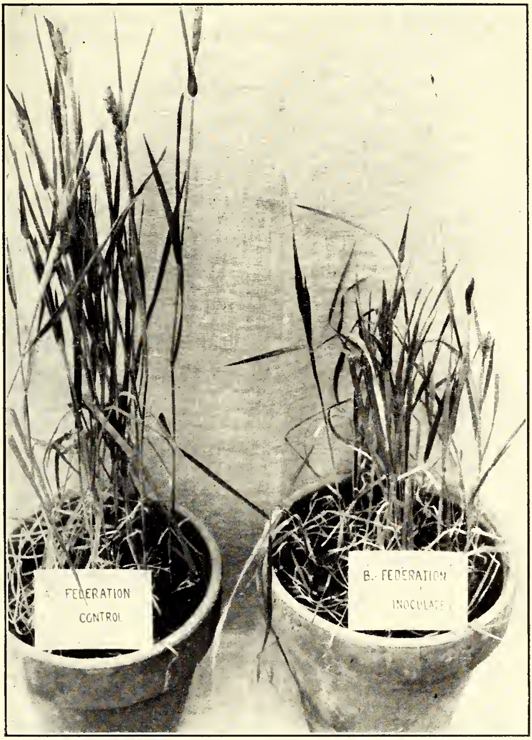

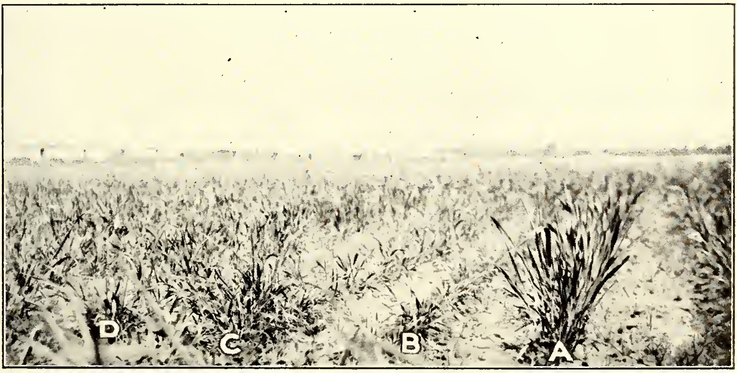


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REVIEW OF THE CARBONIFEROUS STRATIGRAPHY, TECTONICS AND PALÆOGEOGRAPHY OF NEW SOUTH WALES AND QUEENSLAND.

By S. W. CAREY, M.Sc.,
and W. R. BROWNE, D.Sc.

(*Manuscript received, March 11, 1938. Read, April 6, 1938.*)

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I. STRATIGRAPHY.

Proposed Classification.

In a recent paper(7) by one of us (S.W.C.) it was shown that for the Babbinboon area north of Currabubula, on the western limb of the Werrie Syncline, there was amid the freshwater Carboniferous Lower Kuttung beds an intercalation of marine limestone containing a *Lithostrotion* coral-fauna of Viséan aspect; also that some distance above the base of the Burindi Series there was a fauna including the ammonoid *Protocanites* cf. *lyoni* M. & W., a fossil characteristic of a zone low in the Tournaisian.

There is a distinct lithological and facies break at the base of the Lower Kuttung and another break a short distance above the limestone ; it is permissible therefore, to regard the Burindi beds at Babbinboon as approximately equivalent to the Tournaisian and the Lower Kuttung to the Viséan. The Barraba beds, immediately underlying the Burindi, are Upper Devonian.

The Upper Kuttung Series, almost entirely glacial and volcanic, contains in great abundance the *Rhacopteris* flora. The exact time-range of this series is a matter beyond the scope of the present paper, but on the evidence of the plants there appears to be no warrant for supposing it to ascend above Middle Carboniferous. There is thus reason to believe that the sequence commonly called Carboniferous in eastern Australia is equivalent only to a portion of the European Carboniferous system.

The known occurrence of the Viséan coral *Lithostrotion* elsewhere in the State in beds of definite Burindi facies prompted us to examine the records of the Carboniferous sequence. Hitherto it has been generally assumed that a Burindi epoch of marine sedimentation was followed by a Kuttung epoch of terrestrial deposition, but we have been led to the conclusion that during Viséan time in New South Wales marine and terrestrial deposition were going on side by side.

Some revision of the classification is called for, and we propose to modify the generally accepted divisions of the Carboniferous as follows :

Terrestrial.	Marine.	European Equivalents.	
Upper Kuttung Series.	—	Middle Carboniferous (Moscovian).	
Lower Kuttung Series.	Upper Burindi Series.	Viséan.	Lower Carboniferous.
—	Lower Burindi Series.	Tournaisian.	

The names *Kuttung* and *Burindi* are so well known and so entrenched in Australian geological literature that it seems inadvisable to change them ; the former name, too, has always connoted terrestrial and the latter marine deposition, and this significance is preserved in the modified nomenclature. There are no known terrestrial equivalents of the Lower Burindi in this State, but Voisey's work at Drake(23) suggests that the Emu Creek Series in northern New England may be a marine equivalent of the Upper Kuttung Series.

Though there has been as yet but little attempt at zoning the marine beds by their fossil content, it appears to us that most, if not all, of the known Carboniferous in the State can be fitted into the scheme defined above. It will be convenient now to examine this proposition.

New South Wales Correlations.

1. *Great Serpentine Belt.*

The separation of the Carboniferous sequence into a marine (Burindi) and a terrestrial (Rocky Creek) series was one result of Benson's brilliant and extensive field-studies in what he termed the Great Serpentine Belt, stretching along the western margin of New England.(1) Benson showed that on the one hand the Burindi beds merged downwards into the Barraba Series, and that on the other they enclosed lenses of limestone containing a Viséan fauna including species of *Lithostrotion.* The Rocky Creek strata he did not investigate in any detail, they being on the western fringe of the area examined. On a recent visit to the type-area, some 20 miles south-west of Bingara, one of us (W.R.B.) observed the series to be composed mainly of conglomerates and tuffs, with varve-shales on more than one horizon, while near the base an unmistakable tillite was discovered. Incidentally, this is the furthest north point to which Kuttung tillites have been traced. On the eastern side of the Rocky Creek syncline the basal rocks of the series are coarse conglomerates.

In the same area, through the kindness of Mr. Wilfred Crowley, of Pine Cliffs Station, it was possible to examine a small but highly fossiliferous lens of limestone among typical Burindi shales, and probably not more than 200 feet below the base of the Rocky Creek Series. This limestone is from its fossils the stratigraphical equivalent of the Babbinboon limestone and the other Burindi coral-limestones of the Great Serpentine Belt. Dr. Ida Brown has kindly furnished the following list of forms present:

Lithostrotion arundineum Eth. fil., *Amygdalophyllum etheridgei* D. and B., *Aphrophyllum foliaceum* Hill, *Symplectophyllum* cf. *mutatum* Hill.

It is clear from the above that, in the type-area at least, the Rocky Creek Series is Upper Kuttung, the Lower Kuttung is absent and the marine beds embrace both the Upper Burindi and the Lower Burindi Series.

2. *Werrie Syncline.*

The details of the succession have already been described.(7) The Lower Burindi Series is followed by the Lower Kuttung, and the northern end of the syncline is the most northerly point in the State where the Lower Kuttung has been recognized. Where it gives place to the Upper Burindi Series we do not know.

It is of interest to note that recently some fossils collected by Miss E. Basnett from the Lower Burindi beds in por. 179, par. Somerton, have been found by Dr. Ida A. Brown to include the following:

Zaphrentis (*Caninia*) *sumphuens* Eth. fil., *Z.* sp., *Spirifer striata* Sow., *Schizophoria resupinata* Martin, *Productus* spp., *Loxonema* (?) *babinboonensis* Eth. fil. and a Euomphalid. In Europe, the genus *Caninia* makes its first appearance in the *Syringothyris* zone at the top of the Tournaisian, a fact which sets a downward limit to the age of the Somerton beds.

3. *Hunter Valley.*

Both Upper and Lower Kuttung beds have been traced without interruption from a point north of Babbinboon to the southern extremity of the Werrie Syncline at Wallabadah. From here to Scone various elements of both series have been recognized at intervals, and there is no doubt of their continuity. From Scone in a south-east direction to Lamb's Valley and thence eastward to Paterson and Clarencetown the Carboniferous rocks have been mapped and investigated in more or less detail by Osborne(13) (14) and other workers.(3) (10) (19) It is thus possible to assert the physical continuity of both Upper and Lower Kuttung Series over a distance of 150 miles. The most detailed work has been done in the Lower Hunter Valley, and a close comparison is possible between the stratigraphical units developed there and those of the Werrie Syncline, which may be indicated as follows:

Werrie Syncline.	Lower Hunter Valley.		
	Sussmilch.	Osborne.	
Upper Kuttung Series:	Kuttung Series:	Kuttung Series:	
Upper Glacial Stage.	Seaham Beds.	Main Glacial Beds.	Glacial Stage.
Interglacial Stage. Lower Glacial Stage.	Mt. Johnstone Beds.	Main Clastic Zone.	
Lower Kuttung Series	Martin's Creek Beds. Wallarobba Beds.	Volcanic Stage. Basal Stage.	
Lower Burindi Series.	Burindi Series.	Burindi Series.	

The name *Kuttung* was first applied by Sussmilch and David,⁽¹⁹⁾ and the subdivisions of the series for the Lower Hunter Valley were first made by them. These were later renamed by Osborne.

The subdivisions of Osborne's Glacial Stage are closely comparable with those of the Upper Kuttung of the Werrie Syncline. In the latter there are two stages of definitely glacial and fluvio-glacial strata separated by a stage, chiefly tuffaceous, from which glacial evidences are absent. In the Lower Hunter Valley neither Sussmilch nor Osborne definitely recognized a glacial unit in the Mt. Johnstone beds (though the latter noted a horizon of varve-rock at Glenoak), but in the Gosforth area,⁽³⁾ both to the north of Drinan's Mount and between Winder's Hill and Lochinvar, it is possible to recognize the equivalents of the Upper and Lower Glacial and the Interglacial Stage. Further north, in the Muswellbrook area, the Lower Glacial beds are well-developed, and it would seem that all three divisions of the Upper Kuttung Series may be represented.

Of particular interest is the coarse heavy conglomerate, definitely fluvio-glacial or tillitic in places, which everywhere marks the base of the Upper Kuttung Series in the Hunter Valley and which is clearly the counterpart of the "Porphyry Boulder Horizon" in the Werrie Syncline and the heavy basal conglomerates at Rocky Creek.

Nowhere have lava-flows been observed in the Upper Kuttung Series except in the Upper Glacial Stage. The acid lavas in the Werrie Syncline on this horizon may be correlated in a general way with the Paterson toscanite and the felsites which occur at the base of the stage in the

Hunter Valley. The rhyolites and andesites of Pokolbin and Mt. Bright and the Paddy's Hill rhyolite north-east of Raymond Terrace apparently belong to the same epoch.

Within the Lower Kuttung Series there is no persistent sedimentary formation which might be used as a datum. In the Lower Hunter Valley the sequence between the Glacial Stage and the Burindi Series has been divided into a Volcanic and a Basal Stage, the former composed mainly of lavas and tuffs, the latter of clastic sediments, chiefly conglomerate. Further up the Hunter Valley the proportion of tuffs to lavas in the Volcanic Stage appears to increase, and the order of succession and relative proportions of the various lava-flows change, so that the distinctive characters of the stage are somewhat obscured. It is possible, however, that some degree of correlation throughout the Lower Kuttung belt may be effected with the aid of the pyroxene-andesite flows which are so very persistent and widespread. They have been traced for 30 miles in a S.S.E. direction in the Werrie Syncline, and have been observed, though not mapped, beyond its southern limit. From the other direction they are known to occur more or less continuously from the Clarencetown area to the neighbourhood of Muswellbrook and Aberdeen. As explained in a previous paper,(7) it is believed that the Lower Kuttung Series as exposed at Babbinboon comprises both Volcanic and Basal Stages of the Lower Hunter. In regard to the Burindi beds of the latter area, although systematic collecting and examination of fossils have not been done, it is of interest to note that the highest of the marine beds, those calcareous mudstones which at Hilldale immediately underlie the basal (Wallarobba) conglomerate of the Lower Kuttung Series, are relatively rich in the distinctive brachiopod *Syringothyris exsuperans*. In Europe this genus gives its name to the zone within which the boundary between Tournaisian and Viséan Series is drawn, and its occurrence in the topmost Burindi beds at Hilldale is in harmony with, and indeed supports, the view that only the Lower Burindi Series is present in this area.

4. *Lower and Middle North Coast.*

But little detailed work has been published in regard to the stratigraphy of this region, but it is known that Carboniferous rocks extend at intervals from a little south of Port Stephens to beyond Kempsey.

(*a*) *Gloucester.*

In 1921 Sussmilch(17) divided the Carboniferous rocks of this district into (*a*) the Kuttung Series (1,750 feet) consisting of rhyolites with some *Rhacopteris* beds and conglomerates ; and (*b*) the Burindi marine series (10,860 feet), mostly mudstones and tuffs, with conglomerates, oolitic limestones and acid lava-flows. Subsequently to the discovery of the marine limestone in the Lower Kuttung at Babbinboon, and to the conclusion stated by one of us (S.W.C.) in regard to the Myall Lakes area, as detailed below, Sussmilch(20) tentatively suggested that the upper portion of the marine series might be contemporaneous with the Lower Kuttung of other areas. He based his suggestion apparently on the unusual thickness of the marine series. A recent hurried reconnaissance of portion of the area by one of us (W.R.B.) in company with Mr. A. H. Voisey, M.Sc., made it clear that the sequence as given by Sussmilch requires revision. The following is offered as an alternative interpretation of the section on the eastern wall of the valley of Barrington River north-west of the Gloucester Buckets :

Upper Kuttung (" Kuttung " of Sussmilch).	Felsite flow. Tuff, conglomerate and cherty plant-beds (thick). Rhyolite. Plant-beds (?).
Lower Kuttung (" Upper Burindi " in part of Sussmilch).	Bed with marine fossils. Rhyolite. Marine bed with brachiopods. Tuff. *Productus barringtonensis* bed. Tuff. Rhyolite. Tuff. Rhyolite.
Lower Burindi.	Great thickness of shale, mudstone, etc., with oolitic limestones.

This sequence is qualitative only, and is based on a rapid traverse, so that some units may have been missed. The beds here grouped as Lower Kuttung consist predominantly of tuffs and lavas. In contrast to the characteristic hard and compact bluish-green Burindi types the tuffs are light-coloured and contain, as Sussmilch notes, " abundance of quartz and felspar grains, more rarely a little biotite and occasional fragments of rhyolite ". Anyone familiar with the Carboniferous lithology of the Hunter Valley would immediately pronounce this to be a typical freshwater Kuttung and not a Burindi sequence, though the absence of andesite and the prominence of acid types among the lavas are unusual. The marine beds are all thin, but the quantity of colluvial débris on the steep slopes gives a deceptive appearance of thickness. It seems most fitting to interpret this as essentially a terrestrial series with narrow marine intercalations.

No detailed work has been done on the palæontology of these marine beds, apart from the identification and description of the large brachiopod *Productus barringtonensis*, which is very abundant in one bed. This is an endemic species, but is not improbably the Australian representative of some of those large Productids which flourished in Europe near the close of Viséan time.

The boundary between Upper and Lower Kuttung is somewhat arbitrary, but is perhaps justified by the fact that the greatest development of the *Rhacopteris* flora is elsewhere found in the Upper Kuttung beds. The chemical composition of the topmost lava-flow as given by Sussmilch separates it sharply from the lower rhyolites and allies it very closely to the Upper Kuttung rhyolite of Mt. Bright. The thickness of this Upper Kuttung Series seems to have been considerably underestimated.

No glacial or fluvio-glacial rocks were noted in this section, but a cutting on the Rawdon Vale Road, about 6 or 8 miles south of Gloucester, reveals definite varve-shales, with conglomerates and other rocks, underlying rhyolite.

It would appear, then, that conditions at Gloucester were somewhat similar to those obtaining at Babbinboon, though none of the marine transgressions resulted in the formation of coral-limestone.

Incidentally it may be recalled that many years ago Jaquet(10) described alternations of marine and freshwater beds in the Carboniferous between Clarencetown and Gloucester. Both Sussmilch and Osborne have explained the apparent interbedding by faulting, but in view of what is now known there seems a possibility that the original interpretation was in part correct, and that the Lower Kuttung Series may include some marine beds.

(*b*) *Myall Lakes.*

One of us (S.W.C.) during the course of a short survey in 1934(6) formed the opinion that the Lower Kuttung Series was missing. There is an extraordinary thickness of marine beds, which may comprise both Lower and Upper Burindi Series, and these are overlain by Upper Kuttung glacial beds with tuffs and acid lava-flows. A palæontological study of the marine beds would probably yield interesting results.

(*c*) *Port Stephens.*

Sussmilch and Clark(18) have described and mapped a number of isolated outcrops of Kuttung rocks, chiefly igneous, on the coast at Port Stephens. Stratigraphical details are somewhat meagre. It is known that both Kuttung and Burindi rocks are present in the area, and the Upper Kuttung is certainly represented, but other correlations are doubtful.

(*d*) *Taree.*

In association with well-bedded mudstones and tuffs there is a crinoidal oolitic limestone from which the corals *Lithostrotion stanvellense* Eth. fil., *Aphrophyllum hallense* Smith, and (?) *Carcinophyllum patellum* Hill have been identified. They are evidently Upper Burindi. The details of the Carboniferous succession in this area are at present being investigated by Mr. Voisey.

(*e*) *Kempsey.*

Voisey(21) (22) has described from this area representatives of both Kuttung and Burindi Series. The former comprise in descending order:

(1) Glacial beds, including tillite, varve-shales and fluvio-glacial conglomerate.

(2) Cherty mudstones and tuffs containing *Aneimites*, etc.

(3) Sandstones, tuffs and breccias of great thickness.

Unfortunately the junction between Kuttung and Burindi beds seems to be a faulted one, and the remainder of the Kuttung sequence is nowhere revealed.

It may be suggested, perhaps, that the sequence detailed above is equivalent to the Upper Kuttung Glacial and

Interglacial stages. From the Burindi beds no distinctive fossils have been recorded.

Queensland Correlations.

Australian geologists are under a deep debt of gratitude to J. H. Reid for his able and sustained efforts to unravel the stratigraphical tangle of the Upper Palæozoic of Queensland. Some years ago his views on the succession and correlation were set forth in a comprehensive and thoughtful paper,(15) in which, among other things, he sought to link up the Carboniferous beds in Queensland and New South Wales. Reid's admirable pioneer work has made possible the more precise correlation here attempted.

On fossil evidence very similar to that adduced for Babbinboon Dr. F. W. Whitehouse has been able to demonstrate(24) that the Rockhampton Series, including the Lion Creek limestone at the top, comprises both the Viséan and the Tournaisian. It is in fact the exact equivalent of the Upper and Lower Burindi Series of New South Wales. The resemblance extends to the considerable developments of oolitic limestone in both States, pointing to a great uniformity of conditions through a very big range of latitude.

By the contained *Lithostrotion* fauna it has been possible to show that Viséan beds are present in a number of localities between the latitude of Rockhampton and the New South Wales border.(9) It is extremely probable that much of south-eastern Queensland was covered by strata of the Rockhampton Series, of which only a few isolated remnants survive.

Much further to the west and occupying the Drummond Range is a considerable area of freshwater beds which apparently are Upper Devonian at the base with *Lepidodendron australe*, but grade up into beds with the Carboniferous plants *L. Veltheimianum* and *Aneimites austrina*. Reid(15) argues that the upper part of the Drummond Range Series is Lower Carboniferous and the terrestrial time-equivalent of the Rockhampton Series. On the evidence of the *Aneimites* it might be regarded as extending into Middle Carboniferous, but there appear to be tectonic reasons against this.

The Star Beds farther north are believed to be in part Lower Carboniferous.

Of the Upper Kuttung Series Queensland seems to possess equivalents only in the far north at Silver Valley, in the Herberton district, where there is a series of acid lavas, conglomerates, grits, sandstones, and shales containing *Aneimites ovata*. In marked contrast to the folded Drummond Range beds these rocks are sub-horizontal.

At Stanwell, 15 miles south-west of Rockhampton, the Lion Creek limestone is overlain by the Neerkol Series which carries, according to Whitehouse,(25) a Middle Carboniferous marine fauna, and this and a small occurrence at Mt. Barney,(16) about 6 miles N.N.W. of Mt. Lindesay on the N.S.W. border, are to be linked with the Emu Creek Series of Drake as probable marine equivalents of the Upper Kuttung. The presence of whitish grits in the Neerkol Series overlying the typically bluish-black to green marine mudstones suggests a change to terrestrial conditions towards the end of the Neerkol epoch.

Summary.

From the foregoing facts the following appear to be reasonable deductions :

(1) The Burindi series of New South Wales represent the whole of the Lower Carboniferous of Europe, the Lower Burindi being approximately equivalent to the Tournaisian and the Upper Burindi to the Viséan.

(2) Along a narrow belt of lowland, stretching from somewhere north of Babbinboon to the Lower Hunter Valley and the Williams River, deposition of the terrestrial Lower Kuttung Series proceeded synchronously with the Upper Burindi marine sedimentation.

(3) Temporary transgressions of the sea over the coastal lowlands were responsible for occasional intercalations of marine among the terrestrial Lower Kuttung sediments.

(4) In Middle Carboniferous (Upper Kuttung) time terrestrial deposition, largely glacial, took place from beyond Rocky Creek in the north to the Lower Hunter Valley, and probably all along the North Coast region from the Hunter Valley northwards to a point some miles beyond Kempsey.

(5) A fairly close correlation is possible between the Carboniferous rocks in Queensland and those in New South Wales. In the former concurrent marine and terrestrial sedimentation went on during the whole of Lower Carboniferous time. The condition of affairs is expressed in the following table :

	Europe.	New South Wales.		Queensland.		Dominant Vegetation.
		Terrestrial.	Marine.	Marine.	Terrestrial.	
	Middle Carboniferous.	Upper Kuttung Series.	Emu Creek Series of Drake	Neerkol Series.	Silver Valley Beds.	*Rhacopteris* Flora.
Lower Carboniferous	Viséan.	Lower Kuttung Series (with occasional marine intercalations).	Upper Burindi Series with *Lithostrotion* limestone.	Rockhampton Series with Lion Creek *Lithostrotion* limestone at top and *Protocanites* beds near base.	(*a*) Drummond Range Upper Beds with *Aneimites austrina* and *Lepidodendron Veltheimianum*. (*b*) Upper Star Series with *L. Veltheimianum*. (*c*) Pascoe River beds.	*Lepidodendron Veltheimianum* Flora.
	Tournaisian.	—	Lower Burindi Series with *Protocanites* cf. *lyoni*.			
	Upper Devonian.	—	Barraba Series.	Canoona Series.	Lower part of Drummond Range beds and Star beds with *L. australe*.	*L. australe* Flora.

EARTH-MOVEMENTS AFFECTING THE CARBONIFEROUS ROCKS.

The Carboniferous beds in Queensland and New South Wales were to some extent governed in their deposition and were affected after consolidation by a series of important earth-movements. These have been dealt with briefly by Sir Edgeworth David.(8)

1. Kanimbla Movement.

In the Great Serpentine Belt Benson has demonstrated that there is no evidence of a break between the Upper Devonian Barraba and the Lower Carboniferous Burindi Series; in fact, the two series are almost indistinguishable lithologically. Further west, on the western limb of the Werrie Syncline, one of us (S.W.C.) has found the base of the Burindi Series to be marked by a heavy conglomerate, though there is no observed angular unconformity. This basal conglomerate has been traced by Messrs. Lloyd and Mulholland(12) for 30 miles beyond Babbinboon.

In the region west of the Blue Mts., and indeed over a very considerable area of the State, the Upper Devonian beds were folded along a general north-west direction at the close of Devonian time, during what Sussmilch has termed the Kanimbla epoch. It would appear that this folding did not extend to the Great Serpentine Belt, though there are evidences that it advanced as far east as Gosforth and Pokolbin, in the Lower Hunter Valley. The basal conglomerate at Babbinboon, which evidently wedges out eastwards, was probably derived from the erosion of the land lying to the west, which had been uplifted as the result of the orogeny.

The incidence of this epi-Devonian movement appears to have been confined to New South Wales.

2. Wallarobba Movement.

Next there is evidence of a movement of vertical uplift at the close of Lower Burindi time which raised some parts of the area of marine sedimentation just above sea-level. This is the movement called the *Wallarobba Disturbance* by Sussmilch and David.(19) Its incidence is marked by the change from a marine to a terrestrial (Lower Kuttung) facies along a strip extending from north of Babbinboon to the Lower Hunter Valley. The base of the Lower Kuttung is marked in a number of places from Clarencetown to Babbinboon by heavy conglomerates. Sussmilch has recorded evidence that in the former area the elevation was gradual and oscillatory.

So far as we are aware this movement has not been recognized in northern New South Wales or in Queensland.

3. Drummond Movement.

For New South Wales Benson has shown that in western New England the Lower Devonian (?) Woolomin or Eastern Series has been folded and upthrust from the east against a long belt of Burindi beds, including *Lithostrotion* limestones. Sheets of ultrabasic rock are aligned along the thrust-planes. Other sheets of serpentine are known elsewhere in New England and the North Coast district, as at Solferino, Gordonbrook, Port Macquarie, Mt. George(2) and Tinonee on the Manning River, Ellenborough on the Hastings, and Nowendoc in the Upper Manning country.

Some, at least, of these intrusions were probably contemporary with those of western New England.

The precise epoch of the folding, thrusting and intrusion in the Great Serpentine Belt has been a matter of some controversy. Benson(1) contended that they were late Carboniferous, but his arguments are not altogether convincing. Some years ago one of us (W.R.B.) suggested for the movement a late Burindi age,(4) and, though the premises were somewhat inadequate and, as it happens, partly erroneous, the conclusion may be substantially correct. The top of the Upper Burindi (or Lower Kuttung) Series is the only horizon where there is evidence of a tectonic break in the Carboniferous sequence. In most places where it has been identified the base of the Upper Kuttung Series is marked by a coarse, heavy conglomerate already referred to. In one locality, at Gosforth, this conglomerate rests on the Lower Kuttung Series with a distinct angular unconformity, and Osborne's map and sections of the Clarencetown-Paterson area suggest a similar relation there. Though no structural discordance has been reported elsewhere the violent lithological break is in itself an evidence of some marked crustal disturbance.

A possible interpretation of the facts is as follows:

At the close of Burindi time as a result of pressure from the east there was an orogenic movement whose locus of greatest intensity was somewhere in New England to the east of the Great Serpentine Belt. To the west the pressure was relieved by thrusting, and beyond the fault (which may be called the *Peel* Thrust) the strata were only gently folded. Into the most crumpled and faulted areas sheets of ultrabasic magma were injected. Erosion and injection by granite bathyliths have since obliterated the Burindi and much of the Devonian terrain, and only the overthrust and serpentine-injected Upper Burindi beds and the Upper Kuttung conglomerates are left to tell the tectonic tale.

On the other hand one of us (S.W.C.) holds that the Peel overthrust and the injection of the serpentine may well have occurred during the Hunter-Bowen orogeny at the close of the Kamilaroi Period, as described below. Whether or not this is so, however, it is clear that an interval of tectonic disturbance marked the close of Lower Carboniferous time.

This was something more than a diastrophic epoch. It heralded the sharp decline in New South Wales of the hitherto dominant *Lepidodendron* flora and the marked rise of the *Rhacopteris* flora, which appears but sparingly in the Lower Kuttung beds. Furthermore it was after, and perhaps in consequence of, the elevation of the late Burindi mountains that the glaciation, which had started in Lower Kuttung time, reached its culmination.

Not improbably it was at this time that the Upper Devonian beds near Ashford in north-western New England, which underlie Kamilaroi coal-measures with a right-angled unconformity, were folded.*

In Queensland there appear to be evidences of a late Burindi orogeny.

(*a*) The Devonian Silverwood Series near Warwick,(16a) not far across the border from New England, is overlain by Lower Kamilaroi beds with a sharp angular unconformity. No Carboniferous rocks have been identified in the area, but since it is in the northern continuation of the zone of intense late Burindi folding in New South Wales we think its deformation is most probably to be ascribed to that epoch.

(*b*) In the Drummond Range the Devonian and Carboniferous freshwater beds are folded along submeridional axes for 250 miles, and are unconformably overlain by the Kamilaroi Lower and Upper Bowen Series.(15) North of the Drummond Range the area affected probably included Mt. Wyatt (where apparently Lower Carboniferous freshwater beds rest conformably on folded shallow marine Upper Devonian deposits) and the Star River (where the

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* In this area there appear to be Burindi beds also, but their structural relations to the Devonian and Kamilaroi sediments are unknown.

Upper Devonian beds are folded, but the presence of Carboniferous beds is doubtful). It may also have extended to include the rocks of the Hodgkinson and Pascoe River areas.

Reid has argued that the orogeny started in late Lower Carboniferous time, and if so it would seem to have synchronized with the late Burindi movement in New England. It is highly probable that the folding and concomitant uplift provide the reason for the absence of younger beds in this area. The undeformed condition of the Silver Valley beds, much farther north, suggests that they postdate the folding.

(*c*) In the Stanwell area, south-west of Rockhampton, the Lion Creek limestone at the top of the Lower Carboniferous Rockhampton Series is overlain by the Middle Carboniferous Neerkol Series. Though no angular unconformity has been recorded the younger sequence commences with a heavy conglomerate which Reid regards as indicating a distinct tectonic break.

(*d*) At various places between Ipswich and Rockhampton there are sheets of serpentine in contact with Devonian rocks,(5) the whole association so closely resembling that of New England that it is difficult to resist the conclusion that the ultrabasic rocks belong to the same petrographical province. Further, the Carboniferous Rockhampton Series is, according to Reid and Morton,(15a) conformable with the Devonian in the type-area, so that any diastrophism which affected the latter probably did not occur till after the Rockhampton epoch, when, as in New South Wales, folding under pressure from the east may have been accompanied by injections of ultrabasic magma, particularly along a line close to the western margin of the folded zone.

We are led to suggest that the late Viséan orogeny may have produced two zones of folding in Queensland, an easterly one, of considerable intensity with an axis running roughly from Rockhampton through Brisbane and extending into north-eastern New South Wales, and a westerly one, less intense, in the Drummond Range. In the intervening trough there was ltitle or no folding, and this may account for the angular concordance of the Neerkol Series at Stanwell. It is of interest to note that Bryan in 1925(5) advanced a closely similar hypothesis of the folding which affected the Mesozoic rocks of south-eastern Queensland.

We are fully conscious that our tentative explanation is far from resolving the complexities of the Queensland problem; nevertheless it may, we think, be assumed provisionally that the orogeny under discussion affected three great belts in the Carboniferous geosyncline, in New England, the Drummond Range and the coastal belt of Queensland south of Rockhampton. Reid has suggested the name *Drummond Movement* in connexion with the folding of the Drummond beds, and we consider that the term may appropriately be extended to embrace all the diastrophism of late Viséan time in eastern Australia.

4. Lochinvar Movement.

There was apparently no orogeny at the close of Upper Kuttung time. In both Queensland and New South Wales wherever the lowest Kamilaroi beds are in contact with the highest Kuttung there is local angular conformity. There is, however, considerable regional overlap in the Lower Hunter Valley, and evidence of some vertical movement is seen in the heavy conglomerates at the base of the Lower Kamilaroi Dinner Creek Series at Stanwell (Q.), and in the abrupt change from terrestrial to marine sedimentation in New South Wales. This may be called the *Lochinvar Movement.* It comprised elevation followed by submergence and marine transgression. The complete change in flora from Kuttung to Kamilaroi is presumptive evidence of a considerable time-interval of which no sedimentary record is preserved.

5. Hunter-Bowen Movement.

The Burindi and Kuttung rocks of New South Wales were subjected to a further orogeny. In this the overlying Kamilaroi strata were also involved, and it is generally agreed that it occurred towards the end of Kamilaroi time, commencing about the close of the Upper Marine epoch. The area affected is limited more or less strictly on the west by a thrust-system striking parallel to the Peel thrust and at a distance of about 30 miles from it. This system under various names, has been traced with but little interruption from near Maitland in the Lower Hunter Valley in a general north-north-west direction to beyond the latitude of Gunnedah. Jensen(11) has observed in the Nandewar country a discordance between Kamilaroi and Carboniferous beds in Maule's Creek which may be due to the fault, and a little further north, near the head of Rocky Creek, it is almost certainly present. Thus the fault-system probably runs for upwards of 200 miles before disappearing under the Jurassic rocks of the Great Artesian Basin. As to the geological age of this thrust there is no direct evidence and no consensus of opinion. At its southern extremity it frays out into subsidiary faults, which sharply transgress the trend of the late Palæozoic folds, but for the greater part of its course it is in such striking parallelism with the axes of the folds that in our opinion it cannot but be closely related to them.

The position of the zone of greatest folding is not known, but not improbably it was in the New England area, where there are extensive intrusions of late Palæozoic granite. These extend across to the North Coast district, where also the strata are in places highly tilted. Southward the folding seems to have died out about the Hunter Valley.

It is quite conceivable that as a result of the late Palæozoic thrust from the east there was a renewal of movement along the Peel Thrust, and if so this may explain the schistosity which is so characteristic of the serpentine intrusions. Alternatively, the Peel thrust and the serpentine may belong to this epoch.

Reid has emphasised the fact that in Queensland there is a broad coastal belt which was involved in late Palæozoic folding. The folded zone is injected by granite and bounded westward by crumpling and overthrusting of the Kamilaroi Bowen Series along the eastern limb of the Great Syncline. It is significant that, as pointed out by Reid, this boundary is collinear with the bounding thrust-system in New South Wales. Though there is interruption through the transgression of the Mesozoic strata of the Great Artesian Basin there can be little doubt that continuity is maintained beneath them.

We have thus a wide belt of folded Upper Palæozoic strata, bounded westward by thrust-faults and extending perhaps from Townsville to Maitland—a distance of some 900 miles—in a great curve concave to the west, which in late Palæozoic time seems to have behaved as a tectonic unit under the influence of horizontally-acting forces directed from the Pacific Ocean. (See Fig. 1.)

We propose to call the late Palæozoic orogeny the *Hunter-Bowen Movement.*

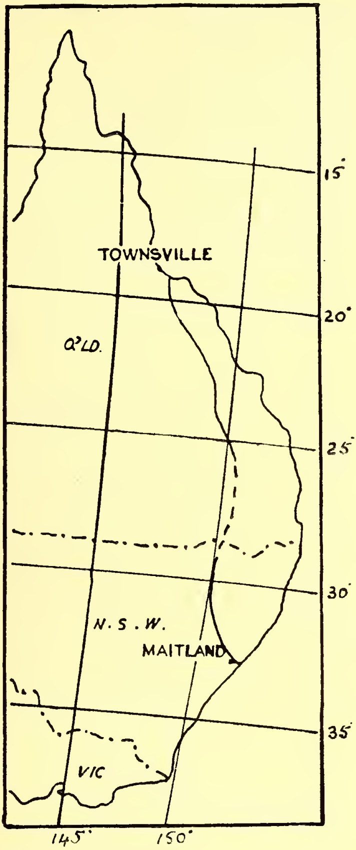

Fig. 1.—Map showing the position of the Hunter-Bowen overthrust zone (the Queensland portion after J. H. Reid).

PALÆOGEOGRAPHY.

In Figs. 2 and 3 an attempt has been made to depict very roughly the marine and terrestrial areas of Burindi and Kuttung time in New South Wales and Queensland.

The Upper Devonian sea, which had stretched far to the west in New South Wales, became very much restricted as a result of the Kanimbla orogeny, and Tournaisian deposition was confined to New England, where Carboniferous sediments were laid down upon the Devonian without unconformity.

The position of the western boundary of this Tournaisian sea is somewhat speculative owing to a cover of later sediments. It must, however, have lain to the east of Pokolbin and Gosforth in the Lower Hunter Valley, where Upper Kuttung rocks rest directly on Devonian granite, and it cannot have been far to the west of the Werrie syncline.

Fig. 2 shows the strip, about 35 or 40 miles wide, which was reclaimed and converted into low-lying lacustrine areas in which the Lower Kuttung lavas and sediments

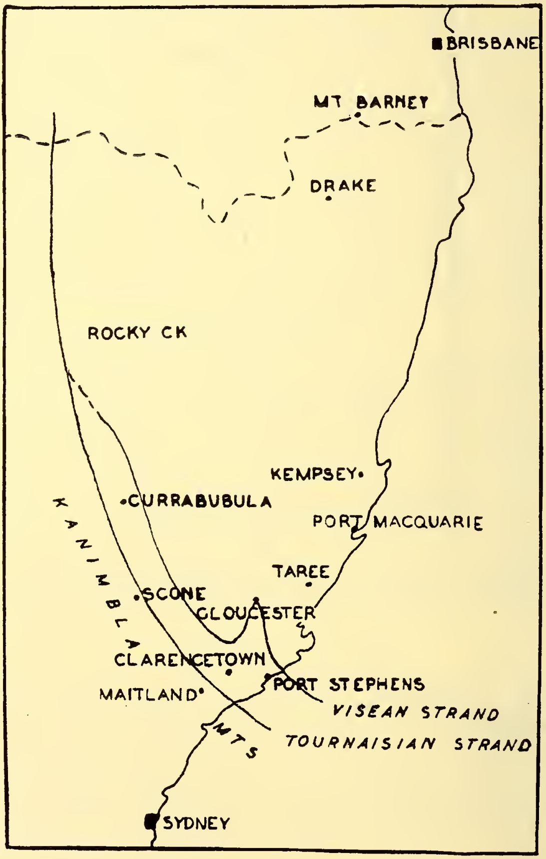

Fig. 2.—Map showing the approximate position of the strand-line in N.S.W. in Tournaisian and Viséan times.

were deposited, while the Upper Burindi (Viséan) sea continued to occupy the area to the east. The volcanic activity may have been related to the crustal movement.

The Drummond Movement at the close of Burindi time drove out the sea from most of the area it had occupied, leaving only a narrow strip in the north-east corner of the State still inundated. New England may have become a broad highland extending into southern Queensland and a scene of active erosion, while a wide, low-lying trough with large lakes occupied the space between this and the

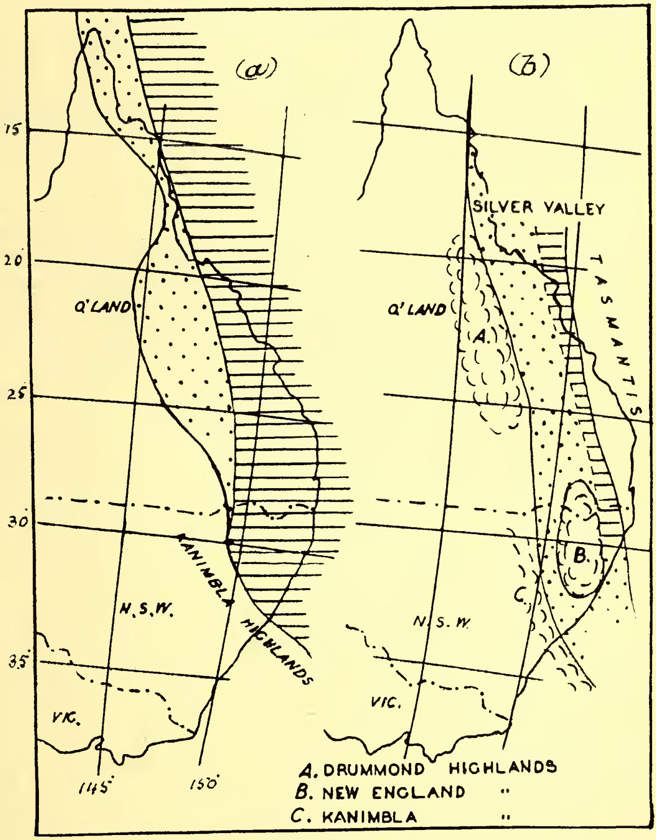

Fig. 3.—Distribution of land and sea in Queensland and N.S.W. (*a*) in Burindi time, and (*b*) in Upper Kuttung time. Land areas blank; marine areas ruled; low-lying areas of terrestrial deposition stippled.

worn-down Kanimbla Mts. stretching north beyond Rocky Creek. This trough became filled chiefly with glacial and fluvio-glacial sediments and volcanic material. To the south in the Hunter Valley it bounded the New England highlands, but south of Newcastle the Kanimbla highlands extended out into what is now the Tasman Sea, and by their erosion supplied débris to the lowlands of the north.

The New England highlands were bounded on the east by another lowland trough which passed through Kempsey and Drake into Queensland. This was occupied in part by the sea and in part by freshwater lakes.

In eastern Australia Upper Kuttung glacial rocks are not known with certainty much farther north than Rocky Creek, N.S.W., and it would appear that the Middle Carboniferous glaciation, though of considerable geological interest, was areally insignificant in comparison with those that followed during the Kamilaroi Period.

In Queensland the boundary between land and sea throughout Lower Carboniferous time ran in some indefinable position between the Drummond Range and Stanwell, possibly somewhere within what is now the Great Syncline. Further north it curved forward to pass east of Silver Valley, where the Upper Kuttung *Aneimites* beds rest on a floor of pre-Carboniferous rocks. Whether the coastline shifted in sympathy with that in New South Wales we cannot say, as Carboniferous strata do not crop out in the area of the Great Syncline. The Drummond Range, with the country north of it perhaps as far as Cape York, formed a low-lying slowly-sinking area of freshwater deposition whose integrity remained unimpaired till the Drummond orogeny converted it into an elevated land-area, the southerly extent of which we do not know.

If folding and uplift of the Lower Carboniferous and Devonian beds between Rockhampton and Brisbane occurred at the time of the Drummond orogeny, the Middle Carboniferous geosyncline must have been restricted to a trough bounded east and west by highlands. The western portion of this—whether terrestrial or marine we know not—may have been continuous with the land trough in New South Wales passing west of New England, while in the east it was occupied by the sea, which stretched south from Stanwell to Mt. Barney and Drake. This long narrow corridor, which separated the mainland of Australia from the land Tasmantis lying to the east, was the sole marine remnant of the Tasman geosyncline which had existed in eastern Australia from Lower Palæozoic time. Further south, where the floor of the trough was a little above sea-level, the lands were precariously united for a time until the rising tide of the Lochinvar inundation severed them once again.

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CHANGES IN AND AROUND THE POUCH IN TRICHOSURUS VULPECULA, AS OCCURRING NATURALLY AND AS THE RESULT OF THE ADMINISTRATION OF ŒSTRONE.

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(With Plates XIV-XV.)

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The silver-grey or long-eared possum, *Trichosurus vulpecula*, is a typical marsupial in that the female of the species possesses a pouch in which it rears its young. Whilst in this laboratory various marsupials were being examined with regard to their response to sex hormones, the female of the commonly occurring possum was injected with œstrone. At our disposal were four fully matured animals which had borne young. Further, we were able to study six fully grown females which had not yet reached sexual maturity, and a number of pouch embryos. All these possums were obtained in the neighbourhood of Sydney, New South Wales.

Observations at the Different Stages of Development.

In the hairless female pouch embryo the pouch is already evidenced by a linear furrow which leads into a small recess behind a semilunar fold opening cephalad (Plate XIV). As the animal grows, the pouch area becomes less evident, and on casual examination of the ventral surface of the almost fully grown or fully grown but sexually immature animal nothing very conspicuous is observed. The colour of the hair is white, becoming grey as the lateral surface and neck are approached. On manual examination, however, and brushing aside of the hair of the lower abdomen, a dry linear furrow is noticed ; the length of this is about 3 cm. and on stretching it opens up to about 1·5 cm. in width. The bottom of this furrow is covered with a small amount of white lanugo-like hairs. On either side of the lower end of the furrow is a white nipple of about 1 mm. in length; in one animal the nipples were retracted. In all these cases no mammary tissue was palpable, and the distal limitation of the furrow was indefinite.

It must be emphasized that in two of these young animals no specially characteristic colorations could be found about the chest, the remainder—including those which had borne young—showing a dark brown streak (*ca.* 2×0·5 cm.) over the sternum.

Three fully grown animals which had not borne young and had been brought to the laboratory in the months of January and February showed a small but distinct pouch. The nipples were slightly enlarged, and the deposit of dark brown pigment could be seen toward the periphery of the pouch and on the nipples. In one instance both nipples were actually capped with the pigment. The hairs on the ventral aspect showed an irregular yellow discoloration.

Four female possums, which had borne young once or several times, were also examined. In these animals, in the place where the opening of the pouch is situated, a golden-brown or dark brown streak of about 4·0 to 6·0 cm. in length was observed, and the fur around it was irregularly stained a brownish-yellow colour. On manual examination, a marked pouch opening cephalad was noted where the deeply coloured streak was seen. This pouch, on stretching, readily admitted the terminal phalanges of two fingers at least. From the fundus of the pouch a tuft of bright golden hair protruded, and a punctate dark brown pigmentation was noted in the depth of the pouch and particularly on the surrounding margins. A single nipple was situated on the lateral recesses of the pouch on each side. They were of unequal size, a fœtus having been attached to the larger one. Beneath the nipples was a plaque-like mammary gland of about 1 cm. in diameter.

In patches the fundus of the pouch was covered with a deposit of a dark brown dry pigment which varied in thickness. In the lateral recesses this deposit was found to reach a thickness of about 0·5 mm. (see Plate XV, *a*). This pigment can be scraped off or removed by scrubbing with a swab soaked in ether. If the swab consists of animal fibre such as wool, then the fibre will be dyed a light dirty brown colour. This coloration, however, is not fast and is readily washed out again with water, although the pigment itself is practically insoluble in water or organic solvents. After removal of the deposit of pigment in the pouch, no reappearance of it was observed during a period of three months.

The fully grown female possums at our disposal were injected with œstrone, the effects of which will be described in the following section.

EFFECT OF ŒSTRONE ON FEMALE POSSUMS.

(A) Sexually Immature Females.

Possum 1. Body weight approximately 2 kilograms. This animal was fully grown but sexually immature. The pouch area, represented by a shallow furrow, was white and covered with fine white hairs. The nipples were retracted and the visible part was about the size of a pin head. They were of a clean white colour. No mammary glands could be felt. There was a dark brown streak of about 2 cm. in length and 0·5 cm. in width over the sternal region. The rest of the hair on the ventral aspect was of a white colour.

On 3.11.37, 900 units of œstrone (B.D.H. œstroform) were administered by intramuscular injection. The animal was inspected again three days following the injection. The ventral aspect in the vicinity of the pouch area then showed a yellowish discoloration. The distal end of the fold representing the pouch had increased in thickness from about one millimetre to about three millimetres and felt quite firm. The hairs in the pouch itself and the skin lining the pouch were still white, but the nipples were capped with a dark brown deposit of pigment, and each nipple, somewhat increased in size, showed a hair-like thread of pigment of about three millimetres in length protruding from the tip of the nipple. No definite mammary tissue could be felt. Eleven days after the injection the condition was the same, except that some of the hairs around the nipples appeared to be also stained by the pigment. The lower margin of the pouch had become lax again and thinner. There was no pigmentation of the skin of the pouch at any time. Two months later the animal still showed a yellow tinge on the hairs over the abdomen. The pouch, however, although being slightly larger, showed no change, and the pigmented threads from the nipples had disappeared.

Possum 2. Body weight 2·25 kilograms. This animal before injection resembled possum 1. Its nipples, however, were not retracted. On 20.10.37, 900 units of œstroform were administered. The day following the injection the ridges bounding the pouch area laterally were larger, due to hypertrophy of mammary tissue, which now formed a plaque surmounted by the nipple. On the sixth day after injection the semilunar fold at the lower end of the furrow was more evident, producing a definite pouch. This structure further increased in size, measuring about 2 cm. in length and 1 cm. in width on the tenth day. About this time a punctate pigmentation was observed, particularly around the hair follicles, and forming a dark brown cap at the tip of the nipples. The hairs in the pouch now had become a rich golden colour. The hair surrounding the pouch was yellowish in colour. Three weeks after injection the pigment scales in the pouch began to disappear, but the nipples were still capped. The hairs around the pouch and in the pouch were still yellowish and golden brown respectively three months later (see Plate XV, *b*).

Possum 3. Body weight 1·6 kilograms. This animal prior to injection presented the features already described in the previous two experiments. The day following the administration of 900 units of œstrone (27.10.37), there was evidence of mammary activity. As in possum 2, this brought the lateral ridges of the furrow more into evidence. With further hypertrophy the nipples tended to recede under the ridge. Within three days of the injection a marked fold similar to that seen in the previous experiments had appeared at the caudal end of the furrow and the nipples were now enlarged. On the sixth day the pouch had increased to 3 cm. in length and 1 cm. in width. On the seventh day the golden brown pigmentation of hairs and of skin had already appeared, being present mostly on the margins of the pouch and over the nipples. On the eighteenth day the pigment on the skin had practically disappeared, and three weeks after injection the lining of the pouch was white again, but the hairs still showed some discoloration. On 28.11.37 a second injection of œstroform consisting of 2,000 units was given. The day following this second injection the pigmentation of the skin had reappeared, being most marked around the nipples, and spreading diffusely into adjacent areas. In the initial stages it bore no relation to the hair follicles. On the third day the nipples were capped with dark brown pigment. This was removed. But the next day the nipples were capped again and during the next ten days fresh pigment was present each day on the tip of the nipples, even though they had been cleaned the previous day. The cleaned nipples had a glistening appearance.

(B) Possums which had Borne Young.

As pointed out previously, such animals may possess a thick deposit of pigment in the pouch. In two animals this pigment was removed and 900 units of œstrone were injected. This small dose produced no obvious changes. Two months later large doses were injected. The results were as follows:

Possum 4. Body weight 2·2 kilograms.

16.2.38. Injected with 12,000 units œstrone.

17.2.38. Nipples are turgid and glistening, but there is not yet evidence of fresh pigment.

18.2.38. Nipples the same as on the previous day. The mammary glands are very hypertrophied, and there are small punctate deposits of fresh pigment throughout the pouch.

19.2.38. The pigmentation is more marked.

20.2.38. The whole pouch is turgid and moist. The brown pigmentation is further increased and covers the whole floor of the pouch. It can readily be removed with the finger as a greasy brown substance which has a characteristic odour faintly resembling musk.

21.2.38. The pouch is still in the same condition as on the previous day. The nipples are glistening, but less firm, and show traces of pigmentation, but no distinct capping.

22.2.38. Both nipples are now capped with a deposit of pigment, and the pigmentation of the pouch in general is increased.

2.3.38. Both nipples are still capped and the pigmentation is still intense. The pigment, however, has lost its oily consistency and is dry. It begins to flake off in layers. The mammary glands are still much enlarged.

DISCUSSION.

The pouch of the female *Trichosurus vulpecula*, as already mentioned, is marked in the hairless pouch embryo (Plate XIV). As the animal grows, the pouch area becomes less evident, partly due to difference in growth rate and partly due to overgrowth of hair, and the distal demarcation becomes indefinite. In the fully grown animal which has hitherto borne no young, there is a spontaneous development of the pouch around the months of January and February. The distal limitation becomes marked and a fine diffuse deposit of pigment appears in the pouch, and the nipples become capped with pigment. The nipples also increase in size, and mammary tissue can be felt.

In Possums 1, 2 and 3, when examined in October and November, the pouch was in the inconspicuous stage. Following the injection of 900 units of œstrone a premature development of the pouch is brought on within a few days, which is comparable to that observed in other young animals occurring in January and February. It appears, therefore, that the injection of œstrone brings on a pouch development which includes mammary gland activity, hypertrophy of the nipples, and secretion of a pigment by the nipples and probably by the tissue lining the pouch. This has further been borne out by experiments on female possums which had borne young and in which the deposit of pigment of the previous breeding season had been removed. After a subsequent injection of œstrone the same train of events occurs, i.e. pouch, nipples and mammary glands become enlarged and a fresh deposit of pigment is laid down. However, in these animals a much larger amount of œstrone is required than in animals which had not borne young, in order to demonstrate the effects of the sex hormone.

Probably the most striking effect observed after the injection of œstrone is the secretion of pigment and the yellow discoloration of the previously white hair on the ventral aspect of the young but fully grown animal. Wood-Jones, in his monograph on the "Mammals of South Australia" (Volume II, Adelaide, 1923), states that the ventral surface of the throat and body and the inner side of the limbs of *Trichosurus vulpecula* are a dirty white, there being usually a slight yellowish-red tinge in the colour. He further states that this yellowish-red colour is accentuated on the chest in the males and around the pouch in the females. Our observations regarding the females of the same species found in the neighbourhood of Sydney agreed with Wood-Jones' description in so far as animals were concerned which obviously were sexually mature. Other females which had not borne young and were probably still sexually immature showed a white ventral aspect. The conditions in the pouch itself have not been commented upon by Wood-Jones or other observers, and the pigment secreted and deposited there, as well as the fact that young females do not possess this pigmentation, has escaped notice. The possibility of a relationship between this pigmentation and sexual development has been suspected. It was investigated by injecting female sex hormone into sexually immature but fully grown possums, and it has been found that the secretion and deposit of pigment can be brought on at will at this stage, as well as in females which had borne young. The pigmentation obtained after an injection of only 900 units of œstrone, however, is much less marked in quantity than that seen occurring naturally in females which have borne young.

The origin of the pigment deposited in the pouch is still obscure, but we have evidence which would indicate that the pigment is secreted by the tissue lining the pouch, and in particular by the mammary glands. This was well brought out in experiments on possum 3, where the pigment which capped the nipples reappeared daily after its removal on the previous day. The secretion itself, which is probably produced in the mammary gland, seems to be initially colourless, as the nipples themselves are white and glistening when the pigmented caps are removed. The secretion, however, soon after it comes in contact with the external environment, assumes a brown colour, and the hairs which come into contact with it while still in its colourless liquid stage are stained varying from a yellow to a deep golden brown. The darkly stained hairs are particularly evident within and on the margin of the pouch. In general, the hairs further from the pouch show only a somewhat irregular yellow discoloration, which diminishes to a certain extent with the degree of distance. This yellow discoloration distant from the pouch may have been brought on by dissemination of the secretion by the animal's snout. In connection with this may be mentioned Wood-Jones' statement that before the young is born the female constantly licks out her pouch.

The secretion after it has become a brown and dry deposit of pigment, has lost the dyeing qualities which must have been present originally, because no animal fibre could be dyed with any degree of fastness with this dry pigment. In support of this theory it may also be mentioned that the pouch embryos at our disposal showed no evidence of staining. This includes also those which already had grown hair. Their ventral aspect is a pure white. The response towards a given amount of œstrone necessarily varies somewhat in the different animals, as shown by these experiments, but it must be borne in mind that the ages of the various animals were not definitely known.

SUMMARY.

The sexually immature Australian possum (*Trichosurus vulpecula*) shows no pigmentation in its undeveloped pouch, and the hair on its ventral aspect is usually white. Injections of œstrone bring on development of the pouch, mammary glands become evident, and the nipples undergo hypertrophy. Simultaneously a pigment is secreted within the pouch and forms a dark brown deposit, while the hairs within the pouch as well as those around it become stained from a yellow to a dark golden brown. Similar changes were observed to occur under natural conditions, and they are considered to be connected with the sex life of the animal.

ACKNOWLEDGMENTS.

The authors wish to express their thanks for access to material to the following: Mr. A. S. le Souef, Curator of Taronga Zoological Park, Sydney; Professor C. W. Stump and Miss M. L. Garde, Department of Anatomy, University of Sydney; and Mr. Ellis le G. Troughton, Zoologist, Australian Museum, Sydney. They are also indebted to The British Drug House (Australia) Ltd. for donating the œstroform used in this investigation.

EXPLANATION OF PLATES.

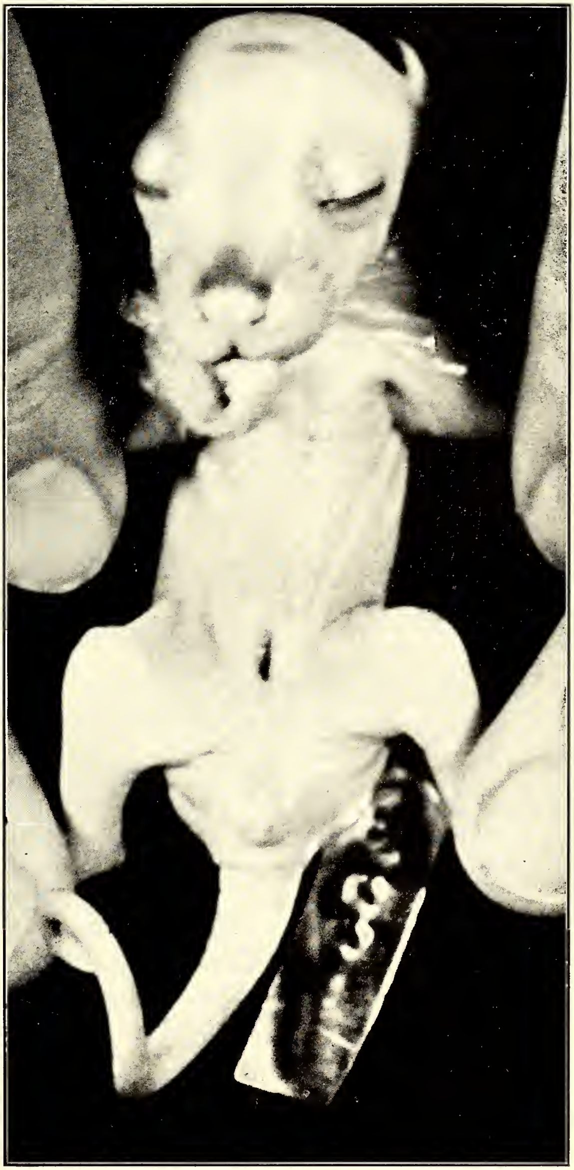
Plate XIV.—Appearance of the pouch in the hairless pouch embryo.

Plate XV.—(*a*) Natural deposit of pigment in pouch of *Trichosurus vulpecula* which has borne young (Possum IV).

(*b*) Possum II, three weeks after injection of 900 benzoate units of Œstroform. Note the nipples capped with pigment and the coloration of the hairs in and around the pouch.

The Gordon Craig Urological Research Laboratories,
Department of Surgery,
University of Sydney.

Journal Royal Society of N.S.W., Vol. LXXI, 1937, Plate XIV.



(*a*)

(*b*)

ABSTRACT OF PROCEEDINGS
OF THE
Royal Society of New South Wales

May 5th, 1937.

The Annual Meeting, being the five hundred and fiftieth General Monthly Meeting of the Society, was held in the Hall of Science House, Gloucester and Essex Streets, Sydney, at 7.45 p.m.

Major E. H. Booth, President, was in the chair. Fifty-two members and visitors were present. The minutes of the general monthly meeting of the 7th April, 1937, were read and confirmed.

The certificate of one candidate for admission as an ordinary member of the Society was read for the second time, and the following gentleman was duly elected an ordinary member of the Society: James Roland English.

The following gentlemen were elected officers and members of Council for the coming year:

President:

W. L. WATERHOUSE, M.C., D.Sc.Agr., D.I.C., F.L.S.

Vice-Presidents:

Major EDGAR H. BOOTH, M.C., D.Sc., F.Inst.P.
R. J. NOBLE, M.Sc., Ph.D., B.Sc.Agr.
A. R. PENFOLD, F.A.C.I., F.C.S.
R. W. CHALLINOR, F.I.C., F.C.S.

Honorary Secretaries:

C. A. SUSSMILCH, F.G.S.
C. ANDERSON, M.A., D.Sc.

Honorary Treasurer:

EDWIN CHEEL.

Members of Council:

E. C. ANDREWS, B.A.
W. R. BROWNE, D.Sc.
Prof. L. A. COTTON, M.A., D.Sc.
Prof. A. P. ELKIN, M.A., Ph.D.
Prof. C. E. FAWSITT, D.Sc., Ph.D.
H. FINNEMORE, B.Sc., F.I.C.
Assoc.-Prof. H. PRIESTLEY, M.D., Ch.M.
H. S. H. WARDLAW, D.Sc., F.A.C.I., Ch.M.
L. L. WATERHOUSE, B.E.
M. B. WELCH, B.Sc., A.I.C.

The Annual Balance Sheet and Revenue Account were submitted to members by the Honorary Treasurer, and on the motion of Mr. Cheel, seconded by Mr. Ollé, were adopted.

THE ROYAL SOCIETY OF NEW SOUTH WALES.

BALANCE SHEET AS AT 31st MARCH, 1937.

LIABILITIES.

1936.		1937.					
£		£	s.	d.	£	s.	d.
	Trust Funds—						
	Clarke Memorial Fund ..	1,697	18	3			
	Walter Burfitt Prize Fund	638	8	2			
	Liversidge Bequest ..	627	8	2			
2,877					2,963	14	7
60	Subscriptions Paid in Advance				3	3	0
—	Sundry Liabilities				35	3	9
150	Provision for Unexpired Proportion of Life Membership Subscriptions ..				153	0	0
26,016	Accumulated Fund				26,261	9	6
£29,103					£29,416	10	10

1936.	ASSETS.	1937.					
£		£	s.	d.	£	s.	d.
	Cash at Bank and on Hand—						
	The Union Bank of Australia Ltd.	237	0	2			
	Commonwealth Savings Bank of Australia	5	0	0			
	Petty Cash	0	12	5			
591					242	12	7
	Commonwealth Bonds and Inscribed Stock—						
	Bonds (Face Value £4,340)	4,291	10	0			
	Stock (Face Value £2,900)	2,947	6	3			
5,282					7,238	16	3
	Science House Management Committee—						
14,540	Payments to date				14,590	0	0
	Sundry Debtors—						
	Subscriptions Unpaid	364	3	0			
	Less Reserve	364	3	0			
1,343					0	0	0
6,800	Library				6,800	0	0
	Furniture	450	5	6			
	Less Sales	4	0	0			
		446	5	6			
	Less Depreciation written off	22	6	3			
		423	19	3			
	Add Additions	28	15	0			
450					452	14	3
	Pictures	53	10	0			
	Less Depreciation written off	2	13	6			
53					50	16	6
	Microscopes	23	15	0			
	Less Depreciation written off	1	3	9			
24					22	11	3
	Lantern	20	0	0			
	Less Depreciation written off	1	0	0			
20					19	0	0
£29,103					£29,416	10	10

The above Balance Sheet has been prepared from the books of account, accounts and vouchers of The Royal Society of New South Wales, and is a correct statement of the position of the Society's affairs on the 31st March, 1937, as disclosed thereby. We have a certificate from the Union Bank of Australia Limited that they hold Commonwealth Bonds to a face value of £4,340 on behalf of the Society, and a certificate from the Registrar of Inscribed Stock that stock to the face value of £2,900 is inscribed in the name of the Society.

HORLEY & HORLEY,
Per CONRAD F. HORLEY,
Chartered Accountants (Aust.).

National Mutual Building,
350 George Street,
Sydney, 22nd April, 1937.

(Sgd.) EDWIN CHEEL,
Honorary Treasurer.

REVENUE ACCOUNT FOR THE YEAR ENDED 31st MARCH, 1937.

PAYMENTS.

Year ended 31st March, 1936. £				Year ended 31st March, 1937. £	s.	d.	£	s.	d.
	2	To Advertising		3	16	0			
	25	,, Cleaning		37	15	0			
	—	,, Depreciation		27	3	6			
	3	,, Electric Light and Gas ..		5	1	8			
	22	,, Insurance		21	11	9			
	—	,, Library Maintenance ..		99	4	0			
	—	,, Loss on Sale of Typewriter		2	0	0			
	64	,, Miscellaneous Expenses ..		66	17	8			
	249	,, Office Salaries and Audit Fees		248	17	0			
	20	,, Office Sundries and Stationery		18	3	1			
	116	,, Printing		65	14	2			
	280	,, Printing and Publishing Journal		282	1	4			
	—	,, Repairs		0	17	6			
	60	,, Stamps and Telegrams ..		53	14	11			
	17	,, Telephone		17	11	2			
		,, Annual Dinner—							
64		Expenses	£73 13 2						
53		*Less* Received	57 7 6						
—	11			16	5	8			
	2	,, Conversazione		—					
							966	14	5
	188	,, Balance, being Net Revenue for the year, transferred to Accumulated Fund					211	5	0
	£1,059						£1,177	19	5

RECEIPTS.

Year ended 31st March, 1936. £	£			Year ended 31st March, 1937. £ s. d.	£ s. d.
	546	By Members' Subscriptions ..			549 3 0
	275	,, Government Subsidy ..			275 0 0
220		,, Science House Receipts ..		171 5 6	
200		*Less* Rent Paid		49 19 6	
—-	20			———	121 6 0
	75	,, Miscellaneous Receipts ..			49 11 6
256		,, Interest Received		280 0 6	
		Less—			
		Clarke Memorial Fund ..	£66 8 0		
		Walter Burfitt Prize Fund ..	24 11 0		
		Liversidge Bequest	24 2 7		
113			———	115 1 7	
—-	143			———	164 18 11
	—	,, Proportion of Life Members' Subscriptions			18 0 0
	£1,059				£1,177 19 5

ACCUMULATED FUND ACCOUNT FOR THE YEAR ENDED 31st MARCH, 1937.

1937—March 31—	£ s. d.
To Arrears of Subscriptions, written off	109 6 0
,, Balance Carried Down	26,261 9 6
	£26,370 15 6

1936—March 31—	£ s. d.
By Balance from Last Account	26,016 13 2
1937—March 31—	
By Amount Received from Estate H. G. Chapman	40 1 0
,, Amount Transferred from Bad Debts Reserve Account	102 16 4
,, Net Revenue for the Year	211 5 0
	£26,370 15 6

1937—March 31—	
By Balance Brought Down	£26,261 9 6

Mr. Penfold proposed and Mr. Sussmilch seconded that Mr. C. F. Horley, of Messrs. Horley & Horley, should be reappointed as the Society's auditor for the year 1937-38. This was the only nomination received, and Mr. Horley was declared elected.

The Annual Report of the Council (1936-1937) was read, and on the motion of Mr. Sussmilch, seconded by Mr. Penfold, was adopted.

Report of the Council (Rule XXVI) for the Year 1936-37.

(May, 1936, to April, 1937.)

We regret to report that we have lost by death nine ordinary members, namely :

Members.	*Elected.*
G. D. Delprat	1921
A. J. Fortescue	1920
Sir A. J. Gould	1897
W. L. Hammond	1909
R. N. Kirk	1919
C. M. McDonald	1935
C. D. Ryder	1907
C. Walker	1910
E. L. Walter	1936

By resignation we have lost ten members, namely :

Member.	*Elected.*
W. N. Benson	1909
E. Breakwell	1917
T. C. Calvert	1909
T. Dunbabin	1935
G. H. Fitzhardinge	1888
L. F. Harper	1913
L. W. O. Martin	1933
H. E. Ross	1895
H. B. Sevier	1918
Gilbert Wright	1917

In addition, seven members have been struck off the roll for non-payment of subscriptions.

On the other hand, nine ordinary members have been elected, namely : Miss E. M. Goulston, A. F. A. Harper, E. E. Hirst, M. R. Lemberg, Mrs. K. M. M. Sherrard, F. Reuter, C. S. Waine, E. L. Walter, H. W. Wood.

One honorary member, Sir Grafton Elliot Smith, died during the year.

Today (28th April, 1937), the membership stands at 279 ordinary members and nine honorary members.

During the Society's year there have been nine general meetings and ten Council meetings. The average attendance at general meetings was 34, and at Council meetings 14.

Thirty-eight papers were read at the monthly meetings ; this is double the number of papers read last year, and the "Journal and Proceedings" for 1936 (Volume LXX) is consequently much larger—about 455 pages, compared with 227 pages in Volume LXIX.

As the time at most of the meetings was fully taken up by the large numbers of papers read, only a few short talks and exhibits were given during the year. The talks delivered were:

"A Geographical Excursion to Eastern Queensland", by C. A. Sussmilch.

"Some Recent Developments in Plastics", by A. R. Penfold.

Exhibits were shown by Mr. D. P. Mellor, Mr. H. H. Baker, Mr. E. G. Bishop and Professor O. U. Vonwiller.

Four Popular Science Lectures were given, as follows:

16th July.—"Soil Erosion and the Use of the Land", by Professor J. Macdonald Holmes.

20th August.—"Bacteria in Relation to Industry", by Mr. E. G. Pont, M.Sc.Agr.

17th September.—"X-Rays and Radium Treatment of Cancer", by Dr. W. H. Love.

15th October.—"Silk, Satin, Cotton, Rags. The origin of certain natural and artificial textiles", by Professor J. C. Earl.

The Annual Dinner was held on Thursday, 29th April, 1937, in David Jones' Auditorium; 110 persons were present.

The Clarke Memorial Lecture for 1937 was delivered on 19th April of this year by Professor H. C. Richards, of the University of Queensland, the title of the lecture being "The Great Barrier Reef of Australia and its Origin".

The Clarke Memorial Medal for 1937 was awarded to Mr. J. T. Jutson, B.Sc., LL.B., of Ivanhoe, Victoria.

In February, 1937, a well-attended public lecture was given under the auspices of the Society by Mr. G. G. Blake, of London. The lecture was entitled "The Electrical Production of Music (Heterodyne Method)".

Meetings of the Science House Joint Management Committee, at which the Royal Society has been represented by Mr. Penfold, Major Booth and Mr. Sussmilch, have been regularly held during the year. As may be seen from the Statement of Accounts, the amount received from Science House has fallen somewhat. This is due to a change in the relative areas occupied by the owner-bodies, leading to a reduction in the rentals paid by them. The amount of rent paid by the Royal Society has been reduced by more than £160 per annum.

The amount of subscriptions due has been reduced during the past year, over £160 of arrears having been collected.

In August of last year Sir Murray Anderson became the Society's Vice-Patron, and it was with deep regret that we learnt of his death only two months later. His Excellency The Lord Wakehurst has recently been invited to accept the position of Vice-Patron.

The Library.—The Council reappointed Professor J. C. Earl and Mr. H. Williams as Honorary Librarians, and they, together with the Executive Committee, were elected as the Library Committee. Two meetings of the Committee have been held during the year.

During the year ended 31st March, 1937, 3,357 accessions have been entered on the catalogue. This is a reduction of 983 from last year's figures, but as 1,600 of last year's accessions were back numbers the number of current periodicals received has been well maintained. Only about 150 back numbers have been received this year; this is to be expected, as our sets have been completed, wherever possible, during the past two or three years.

A few names have been added to the exchange list, and our " Journal and Proceedings " is now sent, as a gift or in exchange, to 353 societies and institutions.

The number of visitors to the library has decreased this year from 183 to 107, but, on the whole, the use made of the library has been satisfactory, compared with previous years. The arrangement with the Australian Chemical Institute for the issue of readers' tickets to their members, for a payment of £10 a year by the Institute, has been continued.

The following amounts have been spent on the upkeep of the library during the year :

Purchase of periodicals	£49 4 9
Binding	49 19 3
	£99 4 0

In November the honorary librarians reported to the Council on the overcrowded condition of the present shelving in the library, and recommended the purchase of at least one additional stack, to be placed on the western side of the library, at right angles to the main body of stacks. The Council agreed to this, and the stack, of eight bays, has now been erected at a cost of £26 10s. This additional shelving space has made possible a better grouping of the periodicals received.

The entries for the Catalogue of Scientific Periodicals in Australian Libraries were sent to the Public Library of N.S.W. during the past year ; over 400 alterations in the entries for the Royal Society were made. The supplement to the Catalogue has not yet been issued.

On behalf of the Council,
E. H. BOOTH,
President.

It was announced that the following Popular Science Lectures would be delivered during the year :

15th July : " French Morocco and its Lessons for Australia ", by Professor T. G. B. Osborn.
19th August :
by R. H. Anderson.
16th September : " Modern Astronomy, and the Changes it has brought about in our Knowledge of the Heavens ", by James Nangle.
21st October :
by Dr. J. G. Churchward.

The following donations were received : 236 parts of periodicals and 19 whole volumes.

The President announced that the Clarke Memorial Medal for 1937 had been awarded by the Council to Mr. John Thomas Jutson, B.Sc., LL.B., of Ivanhoe, Victoria.

The President, Major Edgar H. Booth, delivered his address, entitled " A Special Aspect of Geophysics : Geophysical Prospecting ".

Major Booth, the retiring President, then installed Dr. Waterhouse as President for the year 1937-38, and the latter briefly returned thanks. Dr. C. Anderson proposed a vote of thanks to the retiring President, and this was carried by acclamation.

June 2nd, 1937.

The five hundred and fifty-first General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Dr. W. L. Waterhouse, President, was in the chair. Twenty-seven members and visitors were present. The minutes of the General Monthly and Annual Meeting of the 5th May, 1937, were read and confirmed.

The President announced the death of George R. Cowdery, A.M.I.C.E., a member since 1892.

The following donations were received: 294 parts of periodicals and 25 whole volumes.

The following papers were read:

"Compounds of Creatinine with Alkali Hydroxides", by A. Bolliger, Ph.D.

"A Preliminary Note on the Occurrence of Palæozoic Strata near Taralga, N.S.W.", by G. F. K. Naylor, M.A., M.Sc.

"The Detection and Estimation of α-Phellandrene in Essential Oils", by Arthur J. Birch, B.Sc. (Communicated by Dr. F. Lions.)

Professor L. A. Cotton gave a description, illustrated by lantern slides, of a number of active volcanoes, with special reference to the recent vulcanicity at Rabaul.

An exhibit of "lanital" was supplied by Mr. D. P. Mellor, in whose absence an account of the exhibit was read by Mr. Sussmilch.

Dr. W. R. Browne gave a short talk, illustrated by lantern slides, entitled "The Geological Background of Soil Erosion".

July 7th, 1937.

The five hundred and fifty-second General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Dr. W. L. Waterhouse, President, was in the chair. Thirty-three members and visitors were present. The minutes of the preceding meeting were read and confirmed.

The certificate of a candidate for admission as an ordinary member of the Society was read for the first time.

The following donations were received: 286 parts of periodicals, and 38 whole volumes.

The Honorary Secretary read a letter from the Private Secretary to Lord Wakehurst, stating that His Excellency would be pleased to grant his patronage to the Society during the tenure of his office as Governor.

The following paper was read :

" Red Compounds formed by Picric Acid and Creatinine in the Presence of Sodium Hydroxide ", by A. Bolliger, Ph.D.

Professor T. G. B. Osborn gave an address, illustrated by lantern slides, entitled " The Biological Background of Soil Erosion ". Mr. Andrews and Professor Elkin also spoke on the subject.

August 4th, 1937.

The five hundred and fifty-third General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Dr. W. L. Waterhouse, President, was in the chair. Twenty members and eight visitors were present. The minutes of the preceding meeting were read and confirmed.

The certificates of three candidates for admission as ordinary members of the Society were read for the first time.

The certificate of a candidate for admission as an ordinary member of the Society was read for the second time. The following gentleman was duly elected an ordinary member of the Society : Charles William Davy Conacher.

The following donations were received : 384 parts of periodicals and 29 whole volumes.

A " talkie " film, entitled " Spanning Space " was shown by courtesy of Amalgamated Wireless (Australasia) Ltd. The film briefly covered all phases of Australian wireless development from a national aspect.

The following papers were read :

" The Virtual Genus of a Curve with a Multiple Point ", by Professor T. G. Room, M.A.

" Pyrroles Derived from Acetonylacetone ", by S. J. Hazlewood, B.Sc., and F. Lions, B.Sc., Ph.D.

" Some Derivatives of Higher Catechol Ethers ", by G. K. Hughes, B.Sc., and F. Lions, B.Sc., Ph.D.

" Some Derivatives of 6 : 7-Dimethoxybenzoparathiazine ", by K. J. Baldick, B.Sc., and F. Lions, B.Sc., Ph.D.

Major Booth then gave a short address on the Life and Work of Marconi.

September 1st, 1937.

The five hundred and fifty-fourth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Dr. W. L. Waterhouse, President, was in the chair. Twenty-seven members and visitors were present. The minutes of the preceding meeting were read and confirmed.

The President announced the death of Sir David Orme Masson, K.B.E., M.A., D.Sc., LL.D., F.R.S., an Honorary Member since 1930.

The certificates of three candidates for admission as ordinary members of the Society were read for the second time. The following persons were duly elected ordinary members of the Society: Rita Harriet Harradence, Arthur John Birch, and Kenric James Baldick.

The following donations were received: 356 parts of periodicals, and 33 whole volumes.

The following papers were read:

"The Structural History of Australia during the Palæozoic", by E. C. Andrews, B.A.

"Note on the Shortt Clock at Sydney Observatory", by H. W. Wood.

"Synthetic Substances Allied to Strychnine", by F. Lions, B.Sc., Ph.D.

"The Synthesis of 2-Aminomethyl-benziminazole and Related Substances", by G. K. Hughes, B.Sc., and F. Lions, B.Sc., Ph.D.

October 6th, 1937.

The five hundred and fifty-fifth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Dr. W. L. Waterhouse, President, was in the chair. Forty-three members and visitors were present. The minutes of the preceding meeting were read and confirmed.

The certificate of a candidate for admission as an ordinary member of the Society was read for the first time.

The following donations were received: 299 parts of periodicals, and 6 whole volumes.

The following papers were read:

"On the Chemistry of the Reaction of Creatinine with 3, 5-Di-Nitro-Benzoic Acid", by A. Bolliger, Ph.D.

"The Viscosities of some Complex Salts in Aqueous Solution", by C. E. Fawsitt and R. W. Stanhope.

"Heterocyclic Compounds derived from Catechol Ethers."

Part i. "Some Derivatives of 6 : 7-Dimethoxyquinoline", by F. Lions, B.Sc., Ph.D.

Part ii. "Some 7 : 8-Dimethoxyquinolines and some 5 : 6 : 7-Trimethoxyquinolines", by J. N. Graves, G. K. Hughes, B.Sc., and F. Lions, B.Sc., Ph.D.

Part iii. "Synthesis of 1 : 2-Dimethoxyacridine", by J. N. Graves, G. K. Hughes, B.Sc., and F. Lions, B.Sc., Ph.D.

"Note on the Exudation of *Araucaria bidwilli*", by A. J. Birch, B.Sc.
"The α-Phellandrene Fraction of Eucalyptus Oils", by A. J. Birch, B.Sc.
"The Geological Structure and Stratigraphy of the Molong-Manildra District", by Germaine A. Joplin, B.Sc., Ph.D., and Alma G. Culey, M.Sc.
"The Causes of Ice Ages", by E. Kidson, D.Sc.

November 3rd, 1937.

The five hundred and fifty-sixth General Monthly Meeting was held in the Hall of Science House, at 7.45 p.m.

Dr. W. L. Waterhouse, President, was in the chair. Thirty-two members and visitors were present. The minutes of the preceding meeting were read and confirmed.

The certificate of a candidate for admission as an ordinary member of the Society was read for the second time, and John Allan Dulhunty was duly elected as a member.

The following donations were received: 300 parts of periodicals and 19 whole volumes.

The following papers were read:

"Bæckeol", by A. R. Penfold, F.A.C.I., and Professor J. L. Simonsen, F.R.S.
"Stratigraphy and Physiography of the Goulburn River District", by J. A. Dulhunty. (Communicated by Dr. W. R. Browne.)
"Derivatives of 9 : 10 Dihydroanthracene", by J. N. Graves, G. K. Hughes, B.Sc., and F. Lions, B.Sc., Ph.D.
"The Pyrolysis of Phenyl Cyclohexenyl Ether", by J. W. Cornforth, G. K. Hughes, B.Sc., and F. Lions, B.Sc., Ph.D.
"The Structure of Origanene", Part i, by A. J. Birch, B.Sc.
"On the Occurrence of Glendonites in N.S.W., with Notes on their Mode of Origin", by H. G. Raggatt, M.Sc.

An exhibit of ergot in gramineous plants was made by Dr. W. L. Waterhouse.

December 1st, 1937.

The five hundred and fifty-seventh General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Dr. W. L. Waterhouse, President, was in the chair. Forty-two members and visitors were present. The minutes of the preceding meeting were read and confirmed.

The certificate of a candidate for admission as an ordinary member of the Society was read for the first time.

The President announced that, owing to his projected visit abroad, Mr. C. A. Sussmilch had resigned from the position of Honorary Secretary, and Professor A. P.

Elkin had been elected by the Council in Mr. Sussmilch's place.

The following donations were received: 318 parts of periodicals and 33 whole volumes.

The following papers were read:

"Notes on the Stratigraphy and Physiography of the Talbragar 'Fish-Bed' Area", by J. A. Dulhunty.

"The Essential Oils of *Eucalyptus Australiana* (Baker and Smith) and its Physiological Forms", Part ii, by A. R. Penfold and F. R. Morrison.

"Studies on Physiologic Specialisation of the Organisms Causing Bunt in Wheat, and the Genetics of Resistance to this and Certain other Wheat Diseases", Part i, "Physiologic Specialisation Studies", by Dr. J. G. Churchward.

"On Some Major Geological Faults north of Raymond Terrace and their Relation to the Structure of the Stroud-Gloucester Trough", by Dr. G. D. Osborne.

"The Constitution of Gmelinol", Part i, by A. J. Birch and Dr. F. Lions.

"Binuclear Isomerism of Diphenyl Type", Part iii, by G. K. Hughes, Dr. F. Lions, J. J. Maunsell and T. Wilkinson.

"Heterocyclic Compounds Derived from Catechol Ethers."

Part iv. "Synthesis of Some Dimethoxybenzacridines", by G. K. Hughes, Dr. F. Lions, F. H. Monaghan and T. Wilkinson.

Part v. "Synthesis of 2 : 3 : 6 : 7-Tetramethoxycarbazole and Some Dimethoxy Carbazoles", by G. K. Hughes, Dr. F. Lions, J. J. Maunsell and L. E. A. Wright.

"The Nitration of 2-Methoxydiphenyl Ether", by Dr. F. Lions and A. M. Willison.

"Derivatives of 5 : 6-Indeno (2 : 1) quinoline", by G. K. Hughes, Dr. F. Lions and L. E. A. Wright.

"Derivatives of 4-Hydroxyquinoline", by G. K. Hughes and Dr. F. Lions.

"Heterocyclic Compounds Derived from 5- and 8-Aminoquinolines", by S. J. Hazlewood, G. K. Hughes and Dr. F. Lions.

"Researches on Indoles":

Part iv. "The Utilisation of the Japp-Klingemann Reaction for the Preparation of Substituted Indole Carboxylic Acids", by G. K. Hughes and Dr. F. Lions.

Part v. "Coumarono (3, 2-b) Indole and Derivatives", by J. W. Cornforth, G. K. Hughes, Dr. Lions and R. H. Harradence.

Part vi. "Application of the Fischer Synthesis to Some Cyclohexyl Ketones", by G. K. Hughes and Dr. F. Lions.

April 6th, 1938.

The five hundred and fifty-eighth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Dr. W. L. Waterhouse, President, was in the chair. Twenty-nine members and visitors were present. The minutes of the preceding meeting were read and confirmed.

The President announced the deaths of Mr. Charles W. D. Conacher, a member since 1937, and Professor Walter Howchin, an honorary member since 1934.

The certificates of three candidates for admission as ordinary members of the Society were read, two for the first, and one for the second time. The following gentleman was duly elected an ordinary member of the Society: Gordon Kingsley Hughes.

The President announced that the Clarke Memorial Medal for 1938 had been awarded to Professor H. C. Richards, D.Sc., Professor of Geology in the University of Queensland.

The following donations were received: 983 parts of periodicals, and 103 whole volumes.

The following papers were read:

"The Dimorphism of Bispyridine Cobaltous Chloride", by D. P. Mellor, M.Sc., and B. S. Morris.

"Temperature and Specific Gravity of Sea-water between Japan and Australia", by M. Aurousseau, M.Sc.

"An X-Ray Examination of Chillagite", by F. M. Quodling, B.Sc., and S. B. Cohen, B.Sc.

"Studies in Physiologic Specialisation of the Organisms causing Bunt in Wheat and the Genetics of Resistance to this and certain other Wheat Diseases", Part ii, "Genetical Studies", by J. G. Churchward, Ph.D., M.Sc., B.Sc.Agr.

"Review of the Carboniferous Stratigraphy, Tectonics and Palæogeography of New South Wales and Queensland", by S. W. Carey, M.Sc., and W. R. Browne, D.Sc.

"Changes in and around the Pouch of *Trichosurus vulpecula* as occurring naturally and as the Result of the Administration of Œstrone", by A. Bolliger, Ph.D., and A. L. Carrodus, M.B., B.S.

ABSTRACT OF PROCEEDINGS

OF THE SECTION OF

INDUSTRY

Chairman : A. D. Ollé, F.C.S., A.A.C.I.
Hon. Secretary : E. G. Bishop.

Visits were made by members of the Section of Industry to the following firms, factories and works during the year ending April 30th, 1938 :

1937—

June.—Messrs. Peek Frean, Australia Limited, Ashfield.

July.—Amalgamated Wireless (Australasia) Limited, Radio-Electric Works, Ashfield.

August.—Fitwell Products Limited, Leichhardt.

September.—Australia Silknit Limited, Camperdown.

October.—Westinghouse Sales and Rosebery Limited, Waterloo.

November.—Felt and Textiles of Australia Limited, Waterloo.

ABSTRACT OF PROCEEDINGS

OF THE SECTION OF

GEOLOGY

OFFICERS :

Chairman : Dr. A. B. Walkom.
Hon. Secretary : Dr. G. D. Osborne.

Ten meetings were held during the year, the average attendance being 12 members and nine visitors.

1937.

April 16th.—Exhibits : By Mr. E. C. Andrews : (*a*) Gneiss from Hammerfest, Norway ; (*b*) Glaciated pebble from Lake District, England ; (*c*) Ignimbrite from Putaruru, N.Z. ; (*d*) Lava from Herculaneum. By Professor Cotton : Lime-silicate rocks due to metamorphism of limestone by Gabbro from Port Moresby (collected by Mr. S. W. Carey). By Miss F. M. Quodling : (*a*) Tuhualite from Mayor Island, Bay of Plenty, N.Z. ; (*b*) Ignimbrite, variety Wilsonite, from Lichfield, N.Z. ; (*c*) Silky pumice from Lake Taupo, N.Z. By Dr. G. D. Osborne : (*a*) Obsidian and riebeckite-ægyrine-comendites from Mayor Island, N.Z. ; (*b*) Hypersthene andesite from a lahar on Mt. Ruapehu, N.Z. ; (*c*) Crystals of fayalite in cavity of spherulitic rhyolite, near Lake Taupo, N.Z. Also, on behalf of Dr. W. R. Browne, Kuttung tillite and varves from Bingera, the most northerly point in N.S.W., from which Carboniferous glacial rocks have been reported. By Dr. Ida A. Brown : (*a*) *Pentamerus knightii*, Derrengullen Creek, near Yass, N.S.W. ; (*b*) Large *Spongophyllum* ; and (*c*) *Tryplasma princeps* from the Mid-Devonian of the Murrumbidgee district linking that province with the Tamworth district : (*d*) Fish scale from Oakey Creek, Yass ; (*e*) On behalf of Miss Basnett, fossil resembling *Calceola sandalina* of the Northern Hemisphere ; it is possibly a *Rhizophyllum* ; locality, Wellington, N.S.W. By Dr. Germaine A. Joplin : (*a*) Seven specimens illustrating contamination of olivine-gabbro by andalusite-cordierite-schist producing garnetiferous cordierite-norite and other types. Locality, Aberdeenshire, Scotland ; (*b*) Handspecimen showing limestone invaded by tongue of diorite surrounded by zones of reaction, from Ben Bullen, N.S.W. By Mr. A. H. Voisey : (*a*) Internal mould of *Strophalosia Clarkei* from Mt. Faulkiner, Tasmania ; (*b*) *Strophalosia gerardi* (?) from Collinsville, near Hobart. By Mr. T. Hodge-Smith : (*a*) Portion of the Coolac, N.S.W., meteorite ; (*b*) Cassiterite replacing a gasteropod (*Pleurotomaria*) and crinoid stems from Emmaville, N.S.W.

May 21st.—Address by Mr. C. A. Sussmilch, "The Cainozoic History of N.S.W.".

June 18th.—Three short contributions: (*a*) Note on a possible Tholoid intrusion at the Wallabadah Rock, near Murrurundi, by Dr. G. D. Osborne; (*b*) Note on the structure of the Yass-Bowning district, by Dr. Ida A. Brown; (*c*) Note and exhibit of a method of determining the Optic Axial Angle using a 2E stage-goniometer employing Polaroid, by Miss F. M. Quodling.

Exhibit by Dr. Ida Brown of fossil remains of land plants in slates six miles north of Mudgee, N.S.W., resembling (?) *Hostimella* sp., described by Dr. Isabel Cookson from the Silurian of Victoria. Trilobites occur with the remains.

July 16th.—Exhibits: by Mr. E. C. Andrews: Rhodonite ore with löllingite, pyrrhotite, fluorspar in Pb-Ag ore, massive rhodonite in silver-lead ore, manganhedenbergite, garnet "sandstone", manganiferous garnet, pegmatite with green felspar, crystallised rhodonite with PbS, ZnS, fluor, etc., and calcitic ore. All from the Broken Hill district. By Mr. T. Hodge-Smith (representing the Australian Museum): Crystals of apophyllite from the Zinc Corporation Mine, possibly due to action of carbonated waters on wollastonite. By Mr. L. L. Waterhouse: Iridescent chalcopyrite, variety Towanite. By Dr. Germaine A. Joplin: A series of specimens and diagrams to illustrate the China Clay industry of Cornwall, which was described. By Dr. C. Anderson: Crocodilian teeth (*Pallimnarchus pollens*) from Cuddie Springs, N. S. Wales, and the anterior portion of a lower jaw from Gregory River, North Queensland.

August 3rd.—Address entitled "The Tertiary Stratigraphy of the Californian Region, with special reference to the distribution of the Forams", by Professor A. J. Tieje, of the University of Southern California.

August 13th.—Exhibit by Mr. L. L. Waterhouse of facetted and striated pebble from the Irwin River (W.A.) tillite. Also silicified fault breccia from near Mullumbimby, N. S. Wales. Address by Dr. A. B. Walkom, "Some reported occurrences of *Glossopteris* with older floras".

September 17th.—Address by Mr. H. G. Raggatt, "Geological Aspects of Hydro-Electric Investigations in the Wollomombi District near Armidale, N.S.W.".

October 15th.—Mr. H. F. Whitworth gave a demonstration and description of certain microchemical methods in their relation to mineralogical determinations.

November 1st.—Address by Professor F. Debenham of the University of Cambridge, entitled "The Great Ross Barrier and some of its problems".

December 10th.—Address by Professor W. H. Shideler, of the University of Miami, U.S.A., entitled "The International Symposium on Early Man, held at Philadelphia in March, 1937".

ABSTRACT OF PROCEEDINGS

OF THE SECTION OF

PHYSICAL SCIENCE

OFFICERS :

Chairman : G. Hirst, B.Sc.

Honorary Secretary : A. F. A. Harper, M.Sc.

Committee : Professors O. U. Vonwiller, V. A. Bailey, J. P. V. Madsen, G. H. Briggs, Dr. W. H. Love, Dr. E. H. Booth.

Nine meetings were held during 1937, the average attendance being about thirty members and friends.

April 21st.—Professor G. H. Briggs : " Experiences Abroad."

May 5th.—Mr. R. E. Makinson, B.Sc. : " An Extension of Complex Variable Theory, with some Applications to Physics." Read by J. M. Somerville, B.A., B.Sc.

June 16th.—Dr. D. F. Martyn : " Recent Developments in Upper Atmospheric Research."

July 14th.—Professor V. A. Bailey : " On a New Mathematical Theory of Radio-Interaction, and its Verification by means of Recent Experiments in Europe."

August 11th.—Dr. F. E. Williams : " Solar Eruptions."

September 22nd.—Mr. R. H. Healey, M.Sc. : " The Measurement of Low Pressures by means of an Ionization Gauge."

October 6th.—Mr. J. M. Somerville, B.A., B.Sc. : " The Graphical Solution of Ordinary Differential Equations."

October 22nd.—Rev. Father O'Connell, M.Sc., F.R.A.S. : " Stellar Variability."

November 10th.—Mr. Mark Howarth : " The Application of Physics to Wire Manufacture—Some Problems in the Cold Working of Steel."

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