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ROYAL SOCIETY
OF
NEW SOUTH WALES
FOR
1938
(INCORPORATED 1881)

VOL. LXXII

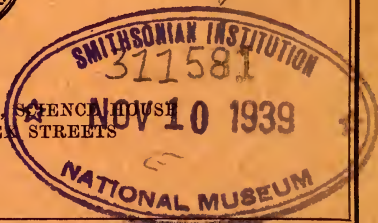
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SYDNEY
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GLOUCESTER AND ESSEX STREETS

1939



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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 $3\frac{1}{2}$ 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 $4 \times 6\frac{1}{4}$ 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	„	„	1878, pp. 324, price 10s. 6d.
„	XII Journal and Proceedings	„	„	1879, „ 255, „
„	XIII „ „ „	„	„	1880, „ 391, „
„	XIV „ „ „	„	„	1881, „ 440, „
„	XV „ „ „	„	„	1882, „ 327, „
„	XVI „ „ „	„	„	1883, „ 324, „
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„	XX „ „ „	„	„	1887, „ 296, „
„	XXI „ „ „	„	„	1888, „ 390, „
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„	XXIII „ „ „	„	„	1890, „ 290, „
„	XXIV „ „ „	„	„	1891, „ 348, „
„	XXV „ „ „	„	„	1892, „ 426, „
„	XXVI „ „ „	„	„	1893, „ 530, „
„	XXVII „ „ „	„	„	1894, „ 368, „
„	XXVIII „ „ „	„	„	1895, „ 600, „
„	XXIX „ „ „	„	„	1896, „ 568, „
„	XXX „ „ „	„	„	1897, „ 626, „
„	XXXI „ „ „	„	„	1898, „ 476, „
„	XXXII „ „ „	„	„	1899, „ 400, „
„	XXXIII „ „ „	„	„	1900, „ 484, „
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„	XLIII „ „ „	„	„	1910, „ 719, „
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„	XLVI „ „ „	„	„	1913, „ 318, „
„	XLVII „ „ „	„	„	1914, „ 584, „
„	XLVIII „ „ „	„	„	1915, „ 587, „
„	XLIX „ „ „	„	„	1916, „ 362, „
„	L „ „ „	„	„	1917, „ 786, „
„	LI „ „ „	„	„	1918, „ 624, „
„	LII „ „ „	„	„	1919, „ 414, „
„	LIII „ „ „	„	„	1920, „ 312, price £1 1s.
„	LIV „ „ „	„	„	1921, „ 418, „
„	LV „ „ „	„	„	1922, „ 372, „
„	LVI „ „ „	„	„	1923, „ 421, „
„	LVII „ „ „	„	„	1924, „ 366, „
„	LVIII „ „ „	„	„	1925, „ 468, „
„	LIX „ „ „	„	„	1926, „ 470, „
„	LX „ „ „	„	„	1927, „ 492, „
„	LXI „ „ „	„	„	1928, „ 458, „
„	LXII „ „ „	„	„	1929, „ 263, „
„	LXIII „ „ „	„	„	1930, „ 434, „
„	LXIV „ „ „	„	„	1931, „ 366, „
„	LXV „ „ „	„	„	1932, „ 601, „
„	LXVI „ „ „	„	„	1933, „ 511, „
„	LXVII „ „ „	„	„	1934, „ 328, „
„	LXVIII „ „ „	„	„	1935, „ 288, „
„	LXIX „ „ „	„	„	1936, „ 528, „
„	LXX „ „ „	„	„	1937, „ 708, „
„	LXXI „ „ „	„	„	1938, „ 396, „
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Royal Society of New South Wales

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M. B. WELCH, B.Sc., A.I.C.

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.
1938		‡Albert, Adrien, Ph.D. (<i>Lond.</i>), B.Sc. (<i>Syd.</i>), A.I.C. (<i>Gt. B.</i>), Acting-Head, Pharmacy Department, University of Sydney; p.r. "Greenknowe," Greenknowe-avenue, Potts Point.
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. (<i>Edin.</i>), C.M.Z.S., Director of the Australian Museum, College-street, Sydney; p.r. 17 Towns-road, Vacluse. (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. <i>Syd.</i> , M.Sc., Ph.D., <i>Cantab.</i> , 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	Arousseau, 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., Professor of Physics in the University of Sydney.

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- 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.
- 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.
- 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 6 Birch, Arthur John, M.Sc., 45 Bickerton-road, Headington, Oxford, England.
- 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 13 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., Department of Geology, University of Sydney, 28 Junction-road, Hornsby.
- 1919 P 1 Briggs, George Henry, B.Sc., Ph.D., F.Inst.P., Officer-in-Charge, Section of Physics, National Standards Laboratory of Australia, University Grounds, Sydney; p.r. 13 Findlay-avenue, Roseville.
- 1935 Brown, Ida Alison, D.Sc., Lecturer in Palæontology, University of Sydney.
- 1913 P 21 Browne, William Rowan, D.Sc., Assistant-Professor of Geology in the University of Sydney. (Vice-President.) (President, 1932.)
- 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.

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1926		Burkitt, Arthur Neville St. George, M.B., B.Sc., Professor of Anatomy in the University of Sydney.
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1923		Cameron, L. D., "Goshen" Private Hospital, Gloucester-road, Hurstville.
1938	P 1	‡Carey, Samuel Warren, M.Sc., Practising Petroleum Geologist, c/o. Australian Petroleum Co., Port Moresby.
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.; 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, K.B.E., Central Square, Sydney
1938		Clune, Francis Patrick, Author and Accountant, 15 Prince's Avenue, Vacluse.
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 3	Culey, Alma Gertrude, M.Sc., 37 Neirbo-avenue, Hurstville.
1912		Curtis, Louis Albert, L.S., F.I.S., v.D., Major, Surveyor, 62 Margaret-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. <i>Syd.</i> , M.D., C.M. <i>Edin.</i> , F.R.C.S. <i>Edin.</i> , Col. A.A.M.C., Comr. Ord. St. John, Medical Practitioner, "Catfoss," 148 Belmore-road, Randwick.
1906		†Dixon, William, "Merridong," Gordon-road, Killara.
1913	P 3	Doherty, William M., F.I.C., F.A.C.I., 30 Hampden-road, Pennant Hills.
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 3	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 20	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. <i>Toronto</i> , 122 Spencer-street, Melbourne.
1935		England, Sidney Willis, 29 Queen-street, Mosman.
1937		English, James Roland, L.S., Water Conservation and Irrigation Commission Survey Camp, Narrandera, 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. <i>Lond.</i> , 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. Taren Point-road, Taren Point.
- 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., Chief Geologist, North Broken Hill Ltd., 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 W. J., 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*), c/o Dept. Education, Sydney.
- 1905 P 6 Harker, George, D.Sc., F.A.C.I.; 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 4 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 Castle-reagh-street, Sydney; p.r. 12 King's-road, Vauchuse.
- 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, Hurlstone Agricultural High School, Glenfield.
- 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, "Linchuden," 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 P 4 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., Box 3010 N.N., G.P.O., Sydney.
- 1929 Jeffrey, Robert Ewen, A.A.C.I., Managing Director, Bardsley's Ltd.; p.r. 9 Greycliffe-avenue, Vacluse.
- 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.), 5 Ithaca-road, Elizabeth Bay.
- 1935 Kelly, Francis Angelo Timothy, 5 Ithaca-road, Elizabeth Bay.
- 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., P.O. Box No. 21, Concord.
- 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 3 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 20 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.*, 49 Oxford-street, Strathfield.
- 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., Box 2968 NN, G.P.O., 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, Navy Office, London, England.
- 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., Pymont.
- 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.
- 1934 Mort, Francis George Arnot, Chemist, c/o Lewis Berger & Sons Ltd., Rhodes; p.r. 16 Grafton-street, Woollahra.

Elected.

- 1879 Mullins, John Lane, M.L.C., M.A. *Syd.*, Barrister, 7 Greenknowe-avenue, Potts Point.
- 1915 Murphy, Robert Kenneth, Dr.Eng., 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 5 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.
- 1938 P 1 Noble, Norman Scott, D.Sc.Agr., M.Sc., D.I.C., Assistant Entomologist, Department of Agriculture, Sydney.
- 1920 P 4 †Noble, Robert Jackson, M.Sc., B.Sc.Agr., Ph.D., Biologist, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. 32A Middle Harbour-road, Lindfield. (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 5 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, Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern; p.r. "Elgarth," Ranger's-road, Cremorne.
- 1938 Powell, John Wallis, A.S.T.C., A.A.C.I., Managing Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern.
- 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 9 Raggatt, Harold George, D.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 P 2 Reuter, Fritz, D.Phil., A.A.I.C., Research Chemist, No. 5, "Wingham," Brighton-boulevard, North Bondi.

Elected.

- 1932 Richardson, Henry Elmar, Chemist, Chase-road, Turramurra.
- 1933 Roberts, Richard George Crafter, Electrical Engineer, 71 Redmyre-road, Strathfield.
- 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, "Araboono," 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.

Elected.

- 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.
- 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," Honebush-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 ‡Susmilch, C. A., F.G.S., F.S.T.C., Consulting Geologist, 11 Appian Way, Burwood. (President, 1922.)
- 1919 ‡Sutherland, George Fife, A.B.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.
- 1932 P 7 Trikojus, Victor Martin, B.Sc., D.Phil., New Medical School, University of Sydney; p.r. 97 Beresford-road, Bellevue Hill.
- 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.
 1935 Vickery, Joyce Winifred, M.Sc., Demonstrator in Botany,
 University of Sydney; p.r. 6 Coventry-road,
 Homebush.
- 1933 P 4 Voisey, Alan Heywood, M.Sc., Lecturer in Geology and
 Geography, New England University College,
 Armidale.
- 1903 P 8 Vonwiller, Oscar U., B.Sc., F.Inst.P., Professor of Physics
 in the University of Sydney. (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.
- 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 4 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, Vacluse. (President, 1925.)
- 1936 Wearne, Harold Wallis, 6 Collingwood-street, Drum-
 moyne.
- 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.
- 1935 Wentworth, William Charles, 17 Wentworth-street,
 Point Piper.
- 1881 †Wesley, W. H., London.
- 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.

Elected.

1921		Willan, Thomas Lindsay, B.Sc., Field Office, Blamo, 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. <i>Lond.</i> , M.R.C.S. <i>Eng.</i> , "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.
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. <i>Edin.</i> , F.R.S., Professor of Anatomy in the University of Cambridge; p.r. 31 Grange-road, Cambridge, England.

OBITUARY 1938.

Elected.

1935 Bayley, Arthur.

1906 Brown, James B.

1888 Kent, Harry Chambers.

1879 Trebeck, Prosper C.

1892 Vickery, George B.

1903 Walsh, Fred.

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.J., 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.
- 1938 Frank Macfarlane Burnet, M.D. (*Melb.*), Ph.D. (*Lond.*), The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.

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.

PRESIDENTIAL ADDRESS

By W. L. WATERHOUSE, M.C., D.Sc.Agr., D.I.C., F.L.S.

(Delivered to the Royal Society of New South Wales, May 4, 1938.)

PART I. GENERAL.

Dr. E. H. Booth in his presidential address last year stated that a feature of the Society's meetings had been the large number of papers read. This year there is an increase of twelve papers to report, bringing the total up to fifty, which is the largest number in the past twenty years, and indeed in the history of the Society, so far as can be ascertained.

The amount set aside for publication of the volume this year was £380. Although so many papers have been published, this amount will not be exceeded, partly because a number of them are short, and partly because special financial arrangements were made to cover the cost of others.

The Council decided to continue the Clarke Memorial Lectures, and the lecture for 1938, which created great interest, was delivered by Dr. C. T. Madigan to a large and appreciative audience, on a subject on which he is one of the authorities, namely "The Simpson Desert and its Borders".

The Clarke Memorial Medal for 1938 was awarded to Professor H. C. Richards D.Sc., of the University of Queensland, who, during the past twenty-five years, has made important contributions to our knowledge of the geology of Queensland.

The Annual Dinner this year was held at the Restaurant Annexe of Messrs. Farmer and Company Ltd., the guest of honour being Sir George Julius. All the arrangements were well carried out, and the comfort and enjoyment of the members and guests were assured.

A notable function in which members of the Society took part was the unveiling of the portrait of the late Sir Edgeworth David, which was hung in the Hall of Science

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House. The ceremony of unveiling the portrait was carried out by Lady David, and the portrait was formally handed over to Science House by Dr. C. Anderson, as Chairman of the Portrait Fund Committee, and accepted by Mr. A. R. Penfold on behalf of the Science House Management Committee. A very representative gathering attended the ceremony. The portrait, which is an excellent likeness, was painted by Mr. Norman Carter, to whom high praise is due for the faithful portrayal, from drawings and photographs, of our honoured colleague.

It is a matter for gratification that, while there are still some arrears of subscriptions outstanding, the total amount of arrears has been further substantially reduced by the efforts of the Honorary Treasurer.

The Balance Sheet shows the position of the Society to be financially sound. It is very pleasing indeed to be able to report that, on the recommendation of the Minister for Education, the Honourable D. H. Drummond, the subsidy from the Government of New South Wales has been restored to £400 per annum.

The library is being further improved by the addition of the stack of shelves for current periodicals which was authorised last year, and these should prove a convenience to members wishing to consult the latest accessions. The arrangements made with Messrs. Tyrrell and Co. for the disposal of a number of superfluous volumes will leave room on the shelves for the current scientific journals, which arrive at the rate of about 300 a month.

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

CHARLES WILLIAM DAVEY CONACHER, died on 30th December, 1937, at the age of 57. Mr. Conacher was a Victorian by birth, but was educated in Edinburgh, returning to Australia in 1916 as General Manager of the North Australia Meat Company and of properties in the north controlled by Vestey's Limited. In 1920 he was transferred to Sydney, and he became, in 1934, General Manager of the Blue Star Steamship Line. Mr. Conacher lived in the Northern Territory for some years, and was considered an authority on its problems. He had a great belief in the future of the Territory, and was keenly interested in all schemes for the improvement of living conditions for the people of the inland, such as the Australian Aerial Medical Services and the Australian Inland Mission. In commercial life Mr. Conacher was

highly esteemed by his colleagues for his wide knowledge of commercial, shipping, and pastoral matters, as well as for the sincerity and integrity of his character. He joined the Society as a life member only last year.

GEORGE ROBERT COWDERY, died on 15th May, 1937, at the age of 77. Mr. Cowdery was born at Glenlee, where his father was engineer-in-charge of the main southern line of N.S. Wales, and came of a railway pioneering family, his grandfather having been associated with George Stephenson in the early days of railways. Mr. Cowdery himself joined the railway service at the age of sixteen, as an apprentice in the locomotive workshops. In 1885 he became the engineer-in-charge of the duplication of the Parramatta to Penrith line, and in 1889, when the railways and tramways became separate departments, he became engineer for tramways, a post which he held for thirty-eight years. He served the two departments for a total period of over fifty-one years, and retired in 1927. When he took charge of the tramways, there were thirty street miles only, laid down in the Sydney system, which was worked by steam traction, with 228 employees. On his retirement the department had 1,547 employees, and the system, which was by that time almost entirely electric, covered 225 street miles—equivalent to 360 miles of single track. Mr. Cowdery had been a member of the Royal Society since 1892.

Two of our very distinguished Honorary Members died during the year.

WALTER HOWCHIN, F.G.S., died at his home in Adelaide on 27th November, 1937, at the age of 91. For more than half a century, Professor Howchin held an important place in the scientific life of South Australia, and the story of his career as a geologist is a romantic one. Born at Norwich in 1845, the son of a Primitive Methodist minister, he received his first schooling at the Academy of King's Lynn, and began work as a clerk in London at the age of twelve years, receiving a salary of two shillings per week, in addition to board and lodging. Later he was apprenticed to a printer, but studied for the ministry, was ordained at the age of twenty, and spent the next sixteen years in places within the Tyne Valley, where the geological features aroused his keen interest in geology. In particular, an abundant glacial till at Haltwhistle led him to a study of glacial action which ultimately resulted in his great

discoveries of evidences of glaciation in Australia. Howchin published a number of geological papers during the years of his ministry in England, and at thirty-three became a Fellow of the Geological Society of London. Ill-health caused him to relinquish his work in the Church, and he came to Australia in the hope of arresting the serious lung trouble which threatened him. He was hardly expected to survive the long sea voyage, and was carried ashore on arrival. On being welcomed by his fellow churchmen of South Australia he referred to the blow that had broken his life at its beginning. A review of his achievements shows that, far from his active life being ended at thirty-six, his most productive period of scientific work was between the ages of sixty and eighty, and his output continued until within a short time of his death.

In 1883 Howchin became a member of the Royal Society of South Australia, and editor of its journal. In 1886, having completely recovered his health, he filled the position of secretary to the Children's Hospital, and later of Lecturer in Mineralogy at the Adelaide School of Mines and at Gawler, at the same time carrying on his studies in the geology, palæontology and mineralogy of South Australia. During his holidays Mr. Howchin visited his friends in the Methodist Ministry, often preaching for them on Sundays, and spending the rest of his time geologising in the surrounding districts. He was always a great walker, even until a few years before his death, and walked long distances collecting specimens and carrying out field observations. In 1902, at the age of fifty-seven, Howchin was appointed Lecturer in Geology and Palæontology at the University of Adelaide, and in the ensuing years he produced a large number of scientific papers, as well as seven books on geography, geology and anthropology. In 1908 he was appointed Honorary Professor of the University of Adelaide, which position he held until his retirement in 1920. It is interesting to record that in his ninetieth year he presented Part I of a new series of geological papers for publication in the Journal of the Royal Society of South Australia.

Among his other activities Professor Howchin was for over twenty years the representative of the Royal Society of South Australia on the Board of the Public Library, Art Gallery and Museum, and later became Honorary Palæontologist to the Museum.

He received the following honours from various societies for his scientific work :

Medal of Royal Society of N.S.W.	..	1907
Mueller Medal of Australasian Assoc. for Advancement of Science	1913
Geological Society of London, Moiety of Lyell Fund	1914
Sir J. Verco Medal of Royal Society of South Australia	1929
Lyell Medal of London Geological Society	..	1934

He was elected an Honorary Member of this Society in 1934.

Professor Howchin's greatest contribution to scientific knowledge is comprised in his series of papers on the existence of glacial rocks in the Adelaide Series of the Mount Lofty Ranges. In many of his researches, particularly those on glacial action, he was closely associated over a period of forty years with the late Sir Edgeworth David, with whom he had much in common.

Australia, and particularly South Australia, owes much to the enthusiasm and unceasing search after knowledge which were characteristic of Professor Howchin throughout his life.

DAVID ORME MASSON, K.B.E., F.R.S., M.A., D.Sc., LL.D., F.I.C., died on 10th August, 1937, in his eightieth year. He was born in Scotland and educated at the Edinburgh Academy, and at the University of Edinburgh. Among his teachers were Crum Brown, and Wöhler of Gottingen. He became assistant to Professor William Ramsay at the Bristol University, and from there returned to Edinburgh University as research fellow in chemistry. In 1886, at the age of twenty-eight, having already distinguished himself by his researches in organic chemistry, he was appointed to the new Chair of Chemistry in the University of Melbourne. The Department of Chemistry went ahead rapidly under his leadership ; his outstanding ability as a teacher soon began to be acknowledged, and research became a recognised part of the work of his school. The Chemistry Department of the University of Melbourne was looked upon as a model, and many of its graduates have had distinguished careers in Australia and abroad, five of them having reached the rank of professor.

Sir David Masson's work did not end in the Department of Organic Chemistry : his wisdom and knowledge were

always available in matters of administration or of service within or without the University. He was President of the Australasian Association for the Advancement of Science from 1912 to 1915, and was one of those responsible for the visit to Australia of the British Association in 1914, and for the holding of the second Pan-Pacific Congress in Australia in 1923. He was closely associated with the Federal Munitions Committees during the Great War, and was one of a group of Melbourne University scientists who designed and tested a respirator for defence against gas, many of the features of which were adopted by the British War Office.

In 1912 Sir David was offered the Chair of Chemistry at University College, London, but elected to remain in Australia, retiring from the Chair at Melbourne in 1923, after serving the University for thirty-seven years. In 1923 he was created K.B.E.

Sir David Masson was keenly interested in the exploration of Antarctica, and was a very active member of the organizing committees of the expeditions. He was asked by the Prime Minister to become chairman of the committee formed to advise the Government on the founding of the Institute of Science and Industry (now the C.S.I.R.), and was one of the founders of the Australian National Research Council, of which he was president from 1922 to 1926. He also founded the Melbourne University Chemical Society, and was a founder and first president of the Society of Chemical Industry of Victoria, as well as founder of the Australian Chemical Institute in 1917. On the incorporation of the last-named society by Royal Charter, Sir David became its first president. Sir David's lectures in chemistry were looked upon as models in their simplicity, clearness, and cultured phraseology. He stood for all that was best in the eyes of his students and his colleagues; and there are many who owe to him the inspiration for their life's work. By the death of Sir David Orme Masson the scientific world has lost one of its most distinguished and cultured minds, whose work and influence have spread far beyond the borders of the Australian Commonwealth. Sir David had been an Honorary Member of this Society since 1930.

PART II.

SOME ASPECTS OF PROBLEMS IN BREEDING
FOR RUST RESISTANCE IN CEREALS.

INTRODUCTION.

In addressing you tonight, I recall that so recently as 1935, Dr. R. J. Noble, in his Presidential Address, dealt with certain aspects of plant disease problems. This had previously been done to a limited extent by Professor R. D. Watt, our President in 1926. Thus in the past twelve years there will have been three of these addresses dealing with agricultural topics.

And yet in a country like Australia, whose wealth is so largely dependent upon its primary products, scientific endeavour may well be directed to the elucidation of some of the many problems in this sphere.

This year we have celebrated the 150th anniversary of the establishment of our colony. The progress made in this period has been stupendous, and brings home forcibly to us the great debt we owe to our pioneers. A continent which was sparsely inhabited by a native race now carries a population of nearly seven millions and produces wealth estimated to amount to £350,000,000 per annum. Without the benefits conferred by science, and particularly in its application to primary production, these tremendous advances would not have been possible. Yet whilst so much has been accomplished by science in the past, much still remains to be done.

Tonight it is my intention to depart somewhat from the general treatment of agricultural problems given by these two past-Presidents, and to deal with certain aspects of the subject of breeding for disease resistance, and more especially rust resistance in cereals. These are days when intense specialisation is a feature in research work, as in other spheres of human activity, and for some time it has fallen to my lot to be concerned with this problem. I hope it may be of interest to you if I review some phases of the work that have been receiving attention, and particularly those dealing with the organisms which cause rust.

ACKNOWLEDGMENTS.

In carrying out the work a great deal of help has been forthcoming from many sources, and I gladly acknowledge

my indebtedness and gratitude to numerous friends; it would be impossible to enumerate all. Drs. E. C. Stakman and M. N. Levine of Minnesota, and Dr. H. B. Humphrey of Washington have been instant in season and out of season in giving help. Officers of the State Departments of Agriculture in Australia and the Council for Scientific and Industrial Research at Canberra have constantly helped, and more particularly those of our own N. S. Wales Department. Of these it is perhaps not invidious to mention especially the generous assistance given continuously by Principal E. A. Southey of Hawkesbury Agricultural College and his officers. Loyal and efficient service has been rendered throughout by Messrs. J. H. Kaye and J. Bolin of the Sydney University attendant staff. Generous financial assistance from the Trustees of the Science and Industry Endowment Fund has been given over a period of years, without which it would have been impossible to carry on the investigations. Grants last year from the Carnegie Research Fund and the Commonwealth Research Fund have enabled much extra work to be done.

HISTORICAL.

Plant breeding goes back to very early days in the history of man. The exact place where man first began to cultivate plants is not known, but it seems certain that Iraq, the site of the traditional Garden of Eden, was one of the earliest homes of civilised man. Here, some thousands of years before the present era, plant improvement was actually practised. It took the form of hand-pollination of the date palm, a procedure which is clearly recorded in certain Babylonian and Assyrian monuments.

Even in those remote times when animals were first domesticated, it was probably recognised that sex lay at the basis of improvement. "Breeding" meant the use of superior animals for mating. Now the fact of sex in plants is less evident than in animals, because in most plants both sexes are present in one and the same plant. In the date palm, however, the sexes occur separately as in domesticated animals. The existence of two sorts of dates was recognised in the early days, viz. sterile and fruit-bearing. Yet the product of the "sterile" male tree was known to be essential for fruit production by the fertile female tree.

Now the seeds from a date palm give rise to male and female trees in about equal numbers. Under cultivation, the growing of such large numbers of "sterile" male trees would be very wasteful of the land. It was early found that if hand-pollination were practised, only a small number of male trees was necessary for the fertilization of a large number of female trees.

Furthermore, it was soon discovered that the offspring could not be depended upon to produce fruit the same as the parent. The fact of variation, which is the basis of plant-improvement work, was thus early recognised.

Mainly by reason of the absence from these regions of such annual crop plants as maize, the fact was lost sight of that all crop plants possess sex, and that wide improvement can be effected by breeding, as with animals. After a long lapse of time, Greek and Roman writers like Aristotle, Herodotus, Pliny, and Theophrastus speculated upon the existence of sex in plants, but made no experiments to determine the facts.

Rudolph Jacob Camerarius in 1694 seems to have been the first to demonstrate by actual experimentation that pollen is indispensable to fertilisation. He further sensed the possibilities in the field of hybridisation, as shown by his comments on his experiments. "The difficult question, which is also a new one, is whether a female plant can be fertilised by a male of another kind, the female hemp by the male hops; the castor bean from which one has removed the staminate flowers, through pollination with the Turkish wheat (maize); and whether, and in what degree altered, a seedling will arise therefrom."

Following upon the establishment of the fact that sex occurs in plants, Linnæus, Kölreuter, Knight, and other hybridists made numerous successful crosses and effected improvements in plants. But the real progress that has been made dates from the commencement of this century, when Mendel's paper, originally published in 1866, was rediscovered. The advances since this time have been tremendous and far-reaching. From haphazard efforts, plant breeding has come to be placed upon a sound scientific basis.

Perhaps in no sphere of plant improvement has greater progress been made than in the work of breeding for resistance to disease. That this is so is a fortunate circumstance for primary producers, faced as they are with a growing host of diseases to combat. The increasing

introduction to Australia of varieties of crop plants from overseas has been responsible for bringing to these shores many serious diseases. This applies with special emphasis to recent times.

LOSSES CAUSED BY PLANT DISEASE.

It is perhaps not amiss to remind you that the losses occasioned by plant diseases are often stupendous. The incidence of disease becomes a limiting factor in crop production in many cases. It has been estimated by Dr. R. J. Noble that plant diseases in Australia cause an annual average loss of £12,000,000. Many records of rust losses in cereal crops have recently been published,⁽⁵⁸⁾ but one or two of them may be repeated here.

For example, in North America the 1935 losses caused by rust in wheat exceeded £60,000,000. Even greater damage, totalling £75,000,000, had been done in 1916. Russian losses in 1934 from the same cause amounted to £32,500,000. Wheat losses in N.S. Wales from rust in 1916 totalled £2,000,000. From the records available it is clear that the ravages of rust in N.S. Wales have caused losses amounting to an average amount of £250,000 per annum during the past twenty years.

HISTORY OF RUST CONTROL.

Various attempts to control rust have been made since early times. Biffen⁽⁷⁾ has reviewed some of these in a recent address. Of the Greeks, Theophrastus (370-286 B.C.) offers notable remarks upon differences in the susceptibility of different cereals to rust. Amongst the Romans, offerings were made at the festival of Rubigalia to ensure rust-free crops. Pliny recommended the early sowing of grain in order that the crops might escape rust. Even in those days it was recognised that climatic conditions played a part in the occurrence of rust epidemics, and that dew settling on the ears was a very important factor in the causation of rust.

Similar philosophies were current in the 17th century. As Biffen reminds us, Worlidge in 1620 suggested the prevention of the noxious dew by the use of smudge fires, or its early removal by two men dragging a cord stretched between them over the uppermost leaves and ears. At this period also, the possibilities were explored of making the crop obnoxious to the "distemper" by placing in it

woollen rags steeped in a solution of salt of tartar, in white wine vinegar, or treated with pepper.

No definite progress was made until a century later. By the middle of the 18th century, farmers had come to recognise that there was some mysterious connection between the barberry and rust epidemics. This led to scattered attempts to eradicate the barberry. It was at this period, also, that there was recognition of the fact that some sorts of wheat were not so seriously affected as were others.

In 1800 an interesting observation was made by Peter Sers in England that spring wheat on his farm was not attacked by rust, although his winter wheat was destroyed. For two decades spring wheats were largely grown, but then they were dropped, probably because of their generally lower yield than winter wheats. Some resistant varieties which were found at this time, e.g. "Little's Anti-mildew", were still in cultivation in parts of England at the beginning of this century.

The discovery of the value of Bordeaux Mixture as a fungicide towards the end of last century did not help the wheat grower in combating rust, although in recent times other protectants like finely ground sulphur scattered from aeroplanes have proved of real value in controlling the disease.

EARLY AUSTRALIAN RECORDS OF RESISTANCE.

In the history of cropping in Australia there are not wanting references to varietal resistance to rust and other diseases. Taking into account the heavy losses that were sustained, this is hardly surprising. It may be of interest to review a few of the records.

As early as 1807 Governor Bligh wrote in a dispatch⁽²¹⁾ dealing with the young colony's crops, "Indian corn is not so liable to the blight and other casualties as attend English grain".

Following upon records of severe rust losses in the wheat crops, it is stated in the *Sydney Gazette* of 1832,⁽⁴⁸⁾ "A new variety which has been introduced by Mr. Cobb has been found to be particularly hardy, and was not affected by smut, although it was grown by the side of Red Lammas, which was much injured by the disease".

Mackellar in 1865,⁽³¹⁾ after calling attention to the fact that indigenous grasses were affected by rust, recorded that so far as wheats were concerned, "Egyptian seven-eared"

and "Egyptian bearded" wheats were not subject to rust.

In the same year a report by Baron F. von Müller was quoted by Schomburgk⁽⁴⁰⁾ to the commission appointed to inquire into the cause of rust in cereals, in the following terms: "Next in importance is the choice of early-ripening varieties and those armed with the strongest coating of an epidermal siliceous deposit, and which are otherwise distinguished for their hardihood". In the same document appears this further statement: "Tuscan wheat imported from Gumeracka, Sth. Australia, turned out very soft and ruined by rust, whilst in the same fields, the English pedigree, Spaldings, red and rough chaff white wheat, remained perfectly free from disease. This singular fact clearly demonstrates that the occurrence of rust is not dependent on climatic conditions alone, but more likely on the effect and reaction of a variety of causes and circumstances, none of them in themselves, perhaps, sufficient to produce the disease. It would point also to an innate susceptibility of certain varieties to suffer from the devastation of the fungus."

Tepper,⁽⁴⁹⁾ in a report published in 1879, says: "At Mount Gambier it was noticed in 1862 that 'creeping wheat', the latest in ripening, was much less affected, if at all, than any other kind".

In Queensland, Tryon⁽⁵⁰⁾ in 1889 refers to the rust damage and states that hard wheats enjoy a comparative immunity from the attacks of the fungus. He believed this to be due to the high silica content of these wheats.

To cite one further reference to these earlier days, William James Farrer made outstanding contributions to the discussions on rust control. He affirmed that he had the greatest faith in the world that the solution to the rust problem could be found in the breeding of suitable varieties of wheat. His labours in this sphere later yielded results of the greatest value to Australia as well as to other wheat-growing countries.

THE USE OF RESISTANT VARIETIES.

Whilst certain remedial measures may be applied in many cases to combat parasites attacking plants, the most effective and most economical measure is to utilise varieties of crop plants which are capable of resisting the parasite. The plant breeder can render invaluable service in making these available. It is probably not too much to say that

breeding for disease resistance is one of the most attractive fields of work in agriculture. This does not mean that correct cultural practices may be neglected. The use of resistant varieties should be supplementary to them.

The starting point in this work of breeding for resistance was the discovery that when a number of wheats were grown together their responses to rust attack were very different. Many proved to be highly susceptible, some moderately susceptible, and perhaps some resistant. Such a search for resistant sorts is often hindered by the fact that rust epidemics do not occur each year. It sometimes happens that a particular variety may mistakenly gain a reputation for resistance; but with the advent of an epidemic it goes down to rust. Rust nurseries in which "artificial epidemics" are produced have proved to be of the utmost value for testing work. And as will become apparent from later considerations, this work must be done locally.

But much more than mere resistance is required. There are many resistant wheats known, but usually they are not cultivated extensively. In addition to being resistant, a variety must have certain other characteristics which make it desirable commercially. For example, it must yield well and must yield a product that is marketable. It is just in this work of combining resistance with the other desired characteristics that the breeder has to play his part.

The next step in the work of controlling rust was the demonstration that resistance was not merely due to external conditions, but was an inherent property of the plant. In turn, this was followed by the epoch-making investigations of Biffen,⁽⁶⁾ who was the first to demonstrate the application of Mendelian principles to breeding for resistance. In passing, it is not without interest to recall that a century previously, T. A. Knight, a pioneer in wheat breeding in England, actually suggested this possibility. Again, W. J. Farrer in Australia had been largely following this method. But Biffen, using almost ideal material in wheats subjected to attacks by the yellow stripe rust, established the fact that resistance and susceptibility were inherited in a simple Mendelian fashion. Further he showed that these were inherited independently of other plant characters, and thus it was possible to make combinations of different characteristics in plants, including resistance.

Consequent upon Biffen's work came a fuller realisation of the value of the Mendelian discovery, and intense activity in the development of resistant plants was the result. As Pearl puts it, "The plant breeder has made Mendelism the working tool of his craft". An indication of the remarkable growth of the subject is shown by the fact cited by Clark⁽¹⁴⁾ that in 1934 there were more than 10,000 publications dealing with plant genetics listed in the U.S.D.A. Library at Washington, D.C.

CONTRIBUTIONS TO WEALTH FROM RESISTANT VARIETIES.

Remarkable contributions towards the control of plant diseases have been made by plant breeders. Coons⁽¹⁷⁾ has recently called attention to some of these achievements. From a careful analysis of results with many crops, he considers that the use of resistant varieties which have been produced in U.S.A. is adding to farm wealth at least 60,000,000 to 70,000,000 dollars a year, and to national wealth a far greater amount.

In the absence of such facilities as are available in U.S.A. for the collection of data of this kind, no such estimate can be made for Australia. But an examination of some of the statistics of the wheat position in N.S. Wales is illuminating. It is only during the past twelve years that figures have been collected relative to the acreage sown with particular varieties of wheat, and hence the available data are rather scanty.

From the official records of the Government Statistician, the following table has been compiled, dealing with some of the best known wheat varieties grown in N.S. Wales.

It should be pointed out that the popularity of a variety depends not upon one thing but upon a number of factors. High productivity is of great importance, but is not the only consideration. Thus in recent years high milling quality has come to be a very needful characteristic in our wheats. Similarly, other features give special values to particular varieties. And it can scarcely be doubted that psychological considerations also enter largely in a number of cases to make a wheat popular.

Now referring to some of the varieties in the table, one can find clear evidence of the effects of successful work in breeding resistant varieties. "Federation" is perhaps the best known production of the late William James Farrer. It marked a wonderful improvement upon the

TABLE I.
Areas in N.S.W. Sown with Specified Varieties of Wheat.

Varieties.	Season.					
	1925-1926.	1929-1930.	1932-1933.	1934-1935.	1935-1936.	1936-1937.
Baringa	—	—	—	38,400	139,619	287,474
Bencubbin	—	—	—	—	25,870	102,977
Canberra	474,797	236,399	91,263	24,947	19,813	16,099
Dundee	—	—	3,587	111,679	278,078	524,237
Federation	853,430	679,043	184,495	54,672	25,314	14,977
Ford	7	3,095	125,291	513,399	761,018	890,959
Hard Federation	158,027	122,946	49,544	20,631	13,547	10,126
Nabawa	155	203,217	1,619,915	1,135,719	997,317	879,688
Pusa 4	1,804	—	51,890	42,393	47,929	67,712
Turvey	190,094	281,556	168,727	62,927	50,991	37,644
Waratah	122,839	817,138	705,890	360,783	329,461	280,410
Yandilla King	182,410	431,512	433,807	200,790	150,612	103,267

wheats previously available. Only twelve years ago it was by far the most widely grown variety, occupying 30% of the total area sown. Since then it has steadily declined to a point at which the latest record shows that it was sown upon only one-third of one per cent. of the wheat area. This falling-off is largely due to the increasing damage done to "Federation" by diseases. The heavy toll taken from it by *Puccinia graminis Tritici* 34 in recent times is a factor of no inconsiderable importance, and its extreme susceptibility to flag smut and other diseases—with the exception of black chaff—has also made it fall into disfavour.

What has been said about "Federation" can be seen to apply to other varieties listed in the table, e.g. "Canberra" and "Hard Federation".

On the other hand there is striking evidence of the rise to popularity of wheats owing to disease resistance. Thus the Western Australian wheat known as "Nabawa", which was sown on a negligible area in 1925, came in seven years to be sown on 32% of the five million acres carrying wheat, and is still almost the most popular variety, occupying more than 20% of the wheat area. In a large measure "Nabawa" came into favour because of its high resistance to flag smut.

A phenomenal rise in popularity is also shown by the South Australian wheat "Ford". From seven golden acres in 1925, the acreage under "Ford" has rapidly mounted, until in the latest census it is found to be the most widely sown of all our varieties, occupying almost 21% of the total area. Here again disease resistance is partly responsible for the increased popularity. "Ford" is the only commercial variety grown which has any resistance of value to *P. graminis Tritici* 34 under conditions favouring rust development. In cases where other varieties have been ruined, "Ford" has given crops.

These illustrations serve to show the value that is placed upon resistant varieties. Results of the same general nature are to be found in crops other than wheat, and give evidence that the plant breeder has added largely to the wealth of our community. Success can be achieved in this work, and the wonder is that there is not a greater intensification of effort in this direction.

CAUSES OF DISEASE.

In order to understand what is involved in breeding for resistance, it becomes necessary to enquire into the nature of disease. In general terms we may say that disease in a plant is anything that interferes with its normal functioning and development. Clearly there must be very numerous causes of disease. They include environmental (or non-parasitic) agents as well as living organisms like fungi which come up for our consideration tonight. Hence the scope of investigations is very wide and it becomes evident that "teamwork" is essential. The plant breeder should work in close cooperation with the plant pathologist and the plant physiologist—not to mention workers in other branches of science. Indeed there are probably few fields of research in which a greater need exists for "teamwork" in the investigations.

Taking first the case of a non-parasitic disease, two distinct factors are involved, viz. the host and its environment. Each necessitates full study, and the interactions of the two must be elucidated. Where, however, the disease is caused by a parasite, the problem becomes more complicated, for there are now three variable factors to be considered, viz. the plant, the environment, and the pathogen. And the interactions of these must be studied. It is seen that plant disease problems present features of great complexity. In ordinary breeding work designed to effect a particular improvement in a plant, the problem is usually straightforward. But in breeding for disease resistance the breeder has to consider not only the genetics of the host, but also the genetics of the pathogen, and these in their relations to each other and to their environments.

THE NATURE OF DISEASE RESISTANCE.

To determine exactly what constitutes resistance to disease is one of the ultimate aims of plant pathological endeavour. Much effort has been expended in work on the problem, but it must be admitted that we are still very much in the dark as to its real nature. A full knowledge would aid the breeder materially in solving his problems of breeding for disease resistance.

I would remind you that resistance to disease in plants is different from that in animals. The animal body with its circulatory systems generally gives a pronounced general reaction to invasion by a parasite. In the plant, on the

other hand, a parasite produces a reaction in an individual host cell or small group of cells. With viruses, of course, the position is different. There is therefore probably no scope for the development of a system of serum therapy in plants. Butler⁽¹²⁾ has recently examined the position, and concludes that analogies between animal and plant diseases should be confined within the limits of cellular pathology. He considers that no evidence has yet been produced to show that in plants anti-parasitic action takes place at a distance remote from the immediate site of infection.

Turning, then, to disease resistance in plants, at the outset it should be pointed out that confusion sometimes exists between disease escape and disease resistance. From a grower's point of view, ability to escape attack by a pathogen is often of the utmost value. Thus the development by Saunders of "Marquis" wheat largely minimised rust losses in Canada and U.S.A. because this wheat matured more rapidly than other sorts that were in cultivation.

Taking an Australian example, one of Farrer's wheats, "Florence", which was bred for resistance to bunt, has been listed as being resistant to *P. graminis Tritici* 34. The fact is that if sown at the right time, this wheat matures so rapidly that it often escapes the damage done to slower-maturing varieties. It has, of course, long been known that its resistance to bunt is due to this same capacity to mature rapidly and grow away from the invading bunt fungus within its tissues. But it has to be remembered that if "Florence" be sown out of season, or if the rate of growth be retarded, it is susceptible to these two parasites.

Resistance is different from escape. It means the possession by the plant of some quality or qualities by reason of which it is capable of resisting attack by the pathogen. It will be evident that such a characteristic is much more valuable than disease escape, and is actually what the plant breeder attempts to incorporate in the variety of crop plant he sets out to synthesise.

So far as the non-parasitic diseases are concerned, there are well-known cases of resistance to them. This also applies to certain of the virus diseases. Numerous instances of resistance to parasitic diseases have been established and some of them carefully investigated. It is clear that in those cases where disease is due to organisms which can be cultured *in vitro* ("facultative parasites") the investiga-

tions are simplified. The metabolism of such parasites can be studied on media of known composition, and from these results information may be obtained which bears upon their capacities as parasites. Work with such organisms has yielded results of the highest value. Brown⁽¹¹⁾ has recently made an able review of the position with regard to them.

In the case of pathogens like cereal rusts ("obligate parasites") which we cannot at present cultivate on any artificial medium, the difficulties are much greater. The living plant is the only known medium upon which such organisms can be grown, and, since such hosts are themselves subject to great variation, the complexities are increased. At the present time it would seem that before real progress can be made in determining the nature of disease resistance to such pathogens, methods will have to be devised of growing them in artificial media.

As a result of many investigations that have been made, it is now generally considered that there are three main types of resistance shown by plants to rust. These are somewhat arbitrary divisions to make, but a classification on this basis is probably helpful as lessening confusion of thought on the subject.

Morphological Resistance.

Morphological resistance was early postulated by Cobb,⁽¹⁵⁾ who considered that tensile strength of the leaves, ratio of sclerenchyma to chlorenchyma, amount of waxy bloom, number and size of stomata, and number and length of leaf hairs, were all related to resistance. Farrer⁽¹⁹⁾ stated that narrow erect leaves with a thick epidermis were important attributes of rust resistance. Ward⁽⁵¹⁾ from extensive investigations upon morphological characters in *Bromus* spp. in their relation to resistance to *P. dispersa* concluded that no such correlation exists. Hursh⁽²³⁾ found that there are marked differences in the amounts and the distributions of sclerenchymatous and chlorenchymatous tissues in the stems of wheats, and, since the rust mycelium is confined to the latter, these anatomical differences formed the basis of the differences between the resistance and susceptibility shown by such wheats. As Hursh puts it, "Rust development is mechanically delimited within certain tissues of resistant wheats". It is interesting that Stakman and Aamodt⁽⁴³⁾ found that fertilisers modified the development of these tissues and

thus altered the resistance or susceptibility of the plants to rust.

Quite apart from the effects upon resistance of such anatomical differences in wheat stems, it has been shown that structural variations in the epidermis may be of importance. Thus varieties like "Kota" and "Webster" have a very thick and tough epidermis. This means that the rust pustules have greater difficulty in bursting through the epidermal layer. The incubation period of the rust is therefore lengthened, and in a given time fewer uredospores will be developed.

Functional Resistance.

Apart from morphological resistance, Hart⁽²⁰⁾ reported that there is functional resistance in some wheats. Since uredospores of rusts gain an entry into their hosts through the stomata, she investigated stomatal movement in relation to rust invasion. She concluded that the early morning habit of delayed opening of the stomata of some wheats, preventing rust entry until the moisture on the plant had evaporated, and the exposure of the delicate germ tubes to desiccation and death, constituted resistance in such wheats. Peterson⁽³⁸⁾ working with stem rust, and Caldwell and Stone⁽¹³⁾ with leaf rust of wheat, consider that stomatal movement is not thus related to resistance. More recently Stakman and Hart⁽⁴⁵⁾ have emphasised that this functional resistance, due to stomatal movement, must not be considered as the only factor making for resistance. It does not apply to all varieties, all rusts, and all conditions. In some circumstances, however, it may be of great importance.

Allen⁽²⁾ considered that the small size of the stomata of some wheats prevented invasion by the rust germ tubes. This would postulate a condition of morphological fixity in the fungus. It is of course well known that in some fungi, e.g. *Synchytrium* spp., naked protoplasm occurs. Brierley⁽⁹⁾ recorded an interesting occurrence in *Botrytis cinerea*. The protoplasm was able, under certain conditions and for a period of time, to live and grow when part of its surface was in a free plasmodial state and only subsequently enclosed within a cell wall. He further states⁽¹⁰⁾ that in another investigation, then being prepared for publication, it was found that certain of the hyphæ of *Botrytis cinerea* were in a naked condition, existing as free protoplasmic substance. This same parasite is known to puncture

mechanically the cuticle of its host plant⁽⁸⁾ by production of a very fine infection peg and thus gain an entry into the tissues. In *P. graminis Tritici* itself it has been shown⁽⁵³⁾ that invasion of the young barberry shoots is brought about by an extremely delicate infection style which punctures the cuticle; once inside the cells the hyphæ resume their normal size. Unpublished work by the author, dealing with *Ustilago hordei* attacking barley, shows exactly this same feature. In view of such cases in which plasticity of the fungus has been demonstrated, it would seem that there is probably some factor other than mere smallness of stomata which has to do with the failure of germ tubes to enter the stomata in these cases.

Physiological Resistance.

Physiological or protoplasmic resistance is the third type and is definitely established. Marshall Ward⁽⁵²⁾ studied the relationship between host and parasite and found that, whilst a rust fungus invaded both susceptible and resistant hosts, the mycelium failed to develop in the latter. This work has been fully confirmed and amplified by other investigators. Whilst such cytological observations can be made readily, their exact interpretation presents considerable difficulty. Many explanations of the apparent physiological incompatibility between host and parasite have been given, but it is probable, as has been pointed out already, that a clear understanding of the happenings awaits development of a satisfactory method of cultivating cereal rusts in artificial media.

Starvation of the hyphæ in the uncongenial host by reason of the death of the host cells was postulated early by Marshall Ward.⁽⁵²⁾ Later there were indications that resistance was independent of nourishment, and that antagonistic relations between host and parasite explained the happenings. On analogy with animal behaviour, it was supposed that toxins were developed. Comes⁽¹⁶⁾ maintained that the acidity of the cell sap was the cause of the resistance, and Hursh produced evidence in support of this view. But Hurd⁽²²⁾ later demonstrated that the differences in resistance could not be related to differences in H ion concentration. Leach⁽²⁹⁾ suggested that the absence of the specific food requirements of a fungus in a resistant host leads to the death of the hyphæ, with consequent secretion of an enzyme injurious to the host cells. Allen⁽²⁾ concluded that in some cases the stomata may shut out

the majority of germ tubes from the uredospores, in other cases heavy contact walls may be laid down subsequent to fungal invasion and prevent further development, and in yet others true immunity from attack may be shown. Newton *et al*⁽³⁵⁾ found that eight wheats, differing widely in rust resistance, showed no corresponding differences in the physico-chemical properties of their expressed tissue-fluids. Newton and Anderson⁽³⁶⁾ demonstrated that phenolic substances, apparently yellow pigments of the flavone type, bear some relation to rust resistance in certain wheats. Later work by Kargopolova⁽²⁶⁾ showed a higher content of proto-catechuic phenols in resistant than in susceptible wheats. Newton and Brown⁽³⁷⁾ point out that the young rapidly growing parts of a wheat plant may be very susceptible to rust, while the older non-mature parts are highly resistant. Johnson and Johnson⁽²⁶⁾ in studies of this phenomenon found that there was no direct relation between sugar content and reaction to rust. Anderson,⁽³⁾ from studies in the inhibitory effects of extracts of different wheats on growth of a rust fungus, concluded that there was no relation between such effects and rust resistance. Johnson and Johnson⁽²⁵⁾ demonstrated that the greater susceptibility of the younger tissues cannot be attributed to a higher organic N content. Anderson⁽⁴⁾ investigated the chemical composition of wheats differing in their reactions to rust, but found no relation between these results and rust resistance. Dufrenoy⁽¹⁸⁾ considers that the resistance is due not so much to pre-existence of phenolic compounds in healthy plants before attack, as to ability of the host to produce such substances as a result of stimulus of the invading fungus. According to recent work by Sukhorukoff and Ovčarov,⁽⁴⁷⁾ resistance to rust in wheats is a direct function of their ammonia content, which, moreover, is an hereditary character of wheat varieties, and is modified by environmental conditions. From work with *P. triticina*, Kargopolova⁽²⁷⁾ states that pyrocatechuic phenols in wheat, under the action of auto-oxidation and of oxidising enzymes, form persistent tannins, the increasing accumulation of which is considered to be one of the most important factors in resistance. Wei,⁽⁵⁹⁾ from studies of resistance of beans to rust, considers that both host and parasite play an active part in the antagonism and the priority of the death of the parasite, or that the host varies from case to case, depending upon the relative production of "toxin" and "antibody", and

relative resistance of both the host and the parasite tissues.

Clearly there is difficulty in reconciling these results. There are undoubtedly a number of different phenomena involved, and, as still further work is done, it is probable that even more will come to light. No one simple explanation of resistance can be expected to cover all cases. It is significant that the plant physiologist and biochemist are working on this problem, and it is reasonable to expect results of the utmost value to a knowledge of rust resistance from workers in these fields. Investigations dealing with growth-promoting and growth-inhibiting substances in plants are opening up new fields.

Alterations in Resistance.

Some of the confusion and controversies that have arisen in classifying plants in regard to resistance have been due to failure to realise what a complex property this is in the plant. Omitting for the present all consideration of the extreme importance of specialisation of the pathogen in its bearing on resistance—a subject dealt with later in this address—some other factors may be referred to briefly.

Whilst it is helpful to consider the three types of resistance as separate qualities, it should be remembered that they may occur together in a particular variety, or one or more of them may be only partially shown. Again the degree of development of a type of resistance is subject to external influences. For example, by increasing temperature and light⁽⁵⁵⁾ it has been shown that physiological resistance may be changed to complete susceptibility in a plant.

It is important to realise that what we call "resistance" may be shown only within a certain range of environmental conditions. For example, if we consider the rust *P. graminis Tritici* 34, a variety like "Federation" is susceptible under practically all conditions. Within a restricted range of conditions, the variety "Ford" is resistant. This range is much wider for "Hope", but nevertheless limited; thus when grown out of season it has been rusted with this race. Certain of the Kenya wheats and some of our own crossbreds, on the other hand, have shown such a wide range of resistance that no susceptibility to *P. graminis Tritici* 34 has been exhibited by them to date, even under the most rust-favourable conditions.

A notable case of the effect of environment was recently shown at Hawkesbury Agricultural College, where a large number of wheats were under test. The rows happened

to be running in a N.E. to S.W. direction, with the paths at right angles to this. In early October, when rather favourable moisture conditions prevailed but temperatures were a little low for full rust development, an inspection of rows from this S.W. end—where the labels were in position—showed hardly any rust. Looked at from the N.E. (sunny) end, the same rows showed heavy rust infection. Examination of individual stems showed striking rust production on the sunny side and absence of it on the shaded side. Later in the season the rust developed on all sides of the stem.

The 1937 season gave a striking illustration of the effect of climatic conditions upon rust development in coastal areas. October is to be regarded as a critical month in this respect. In this year the temperatures were lower than is often the case, although moisture was abundant in the form of heavy dews as well as rainfall. The attacks of *P. triticina* on wheat, and of *P. graminis Avenæ* and *P. coronata* on oats were so heavy as to completely ruin crops. These rusts are known to have a lower optimum temperature for development than *P. graminis Tritici*. Only when the warmer conditions prevailed did stem rust appear in the wheat crops.

The profound effect that reduction of light intensity in certain circumstances may have on rust development has but recently been realised. And again, the concomitant effects of simultaneous infection of the host by rust and by another pathogen have also been shown to lead to susceptibility being shown by wheats which were otherwise resistant.

The foregoing considerations indicate how difficult it is to make accurate observations on resistance, and how complex is the problem of determining what actually constitutes rust resistance in a plant under present limitations of our knowledge. Each case deserves individual study. There is a real need for fundamental studies to provide exact information on the subject, and only when such information is available will it be safe to generalise.

STUDIES OF RUST FUNGI.

In any disease investigation it is a matter of paramount importance to learn the cause of the disease. Fungi are the causal agents of rust. They are very highly specialised organisms having very complex life histories.

Apart from numerous rusts on grasses, the cereal rust fungi known to occur in Australia are the following :

Puccinia graminis Tritici E. and H., causing stem rust of wheat.

P. triticina Eriks., causing leaf rust of wheat.

P. graminis Avenæ E. and H., causing stem rust of oats.

P. coronata Avenæ (Cda.) E. and H., causing leaf rust of oats.

P. graminis Tritici E. and H., causing stem rust of barley.

P. anomala Rostr., causing leaf rust of barley.

P. graminis Tritici E. and H., causing stem rust of rye.

P. dispersa E. and H., causing leaf rust of rye.

It is noteworthy that the yellow stripe rust caused by *P. glumarum* (Schm.) E. and H. and the stem rust of rye, *P. graminis Secalis* E. and H., are not known to occur in Australia. This is but one of many illustrations of the fact that the Australian rust problems demand local study.

In general the stem rusts cause more damage than the leaf rusts, although evidence is accumulating that the latter are much more serious than is often supposed ; whilst they do not lead to such obvious pinching of the grain as do stem rusts, they reduce the number of grains set and so diminish productivity.

1. Stem Rust of Wheat.

Stem rust of wheat is the most important of the group and calls for most attention. In Australia it has been shown⁽⁵⁵⁾ that it is present in the uredospore stage throughout the year, occurring on "volunteer" wheat plants and grasses in between the wheat-growing seasons. It is with us always.

Apart from this uredospore attack of the wheat host, it must be remembered that, despite oft-expressed statements to the contrary, the Australian rust does attack the barberry. That is to say it goes through its complete life history here at least on some occasions.⁽⁵⁷⁾ The grave importance of this lies largely in the fact that new physiological races have been shown to originate on the barberry by hybridisation and segregation.⁽⁵⁶⁾

Physiological Specialisation.

The occurrence of physiological races is a feature of the utmost importance. Physiological specialisation has been known for many years, but its direct bearing upon problems of breeding for disease resistance is sometimes overlooked. Aamodt⁽¹⁾ has aptly said, "To produce new varieties that are not resistant to all the races of the pathogen that are present in the region in which the variety is to be grown is to acquiesce, at least, to only temporary or partial success". The truth of this has been amply confirmed in Australian experience, as will be described later in this address. Many otherwise inexplicable happenings in the work of breeding for rust resistance become perfectly plain when the facts of specialisation are known.

More recently Stakman⁽⁴⁶⁾ has put it this way: "That racial specialisation is important is generally recognised, but how important it is is not universally appreciated. The more the problem is investigated, the stronger becomes the conviction that its importance can scarcely be over-estimated." And again, "The extremists who assert that physiologic specialisation foredooms to failure the breeding of resistant varieties, and those who assume that it is of no consequence, are both likely to impede progress".

A clear illustration of the far-reaching effects of rust specialisation was given in last year's severe epidemic in U.S.A. Dr. Stakman has recorded that this was unusual, in that it had its origin in Southern Mexico. Barberries are common there, and the unusual races found in U.S.A. in this season doubtless were derived from aecidial infections of these plants. The variety "Ceres", which had always been resistant prior to 1935, was again so severely damaged that it will probably go right out of cultivation. The susceptibility is due to the prevalence of race 56, which first had been recorded in 1928 as a barberry derivative in U.S.A. (Parenthetically it should be remarked that this is one of the races recorded in Australia in 1929⁽⁵⁶⁾ as a direct derivative from a barberry inoculated with race 34, and that to date this race has not been found under natural conditions in Australia. Nevertheless natural infections of barberries here by race 34 may well lead to its occurrence in our crops.) The variety "Thatcher" which has been so widely acclaimed for its rust resistance, performed well and is superseding "Ceres", but Dr. Stakman states that even "Thatcher" showed definite signs of serious rust damage,

despite the absence of race 36, and that a more resistant variety than "Thatcher" must be developed.

Determination of Specialisation.

Specialisation is a phenomenon of wide occurrence in many groups of the fungi. The identification of physiological races can be made by several methods, e.g. by the pathogenicity shown by particular host plants, by cultural characteristics on artificial culture media, by physico-chemical reactions, and by biometrical studies.

Amongst the rusts, specialisation can best be demonstrated by the differences shown in their parasitic capabilities on certain selected host plants. Dr. E. C. Stakman of Minnesota is outstanding amongst workers in this sphere, and has been largely responsible for the developments that have taken place. It would be difficult to overestimate the value of his work.

To take an illustration of specialisation, stem rust occurs on wheat and on oats, but the rust on wheat does not attack oats and *vice versa*. Both attack the barberry, but nevertheless retain their identity when reinoculated on to their gramineous hosts. They may thus be regarded as two distinct sub-species. The first has been named *Puccinia graminis Tritici* and the second *P. graminis Avenae*. In all, eight sub-species of *P. graminis* have so far been recorded, and it seems certain that an additional one occurs in Australia. Work on this is not quite complete, but it will probably be recorded as *P. graminis Lolii*.

Now, within these sub-species further separations of different groups may be made. This is best done by culturing each rust on seedlings of a selected set of varieties of the particular cereal host—a so-called "differential set". The wheat stem rust differentials selected by Stakman and Levine⁽⁴²⁾ number twelve, those for oats three, for rye five, and so on. The reactions given by each member of the differential set are recorded. Certain varieties in the set may be resistant to one rust and others susceptible. The tabulation of these results gives a means of identifying that particular rust. It is designated by a number which is written in Arabic numerals after the sub-specific title. Thus *P. graminis Tritici* 34 refers to Physiological Race No. 34 of *Puccinia graminis Tritici*. The differential set has of course been selected empirically. In our work a number of instances have been found in which the addition of yet other varieties to the set makes it

possible to separate two otherwise similar races into different entities.

Now a second series of inoculations of the same differential set with another rust may yield the same results. This shows that the same physiological race is concerned. On the other hand, a different reaction on one or more of the differential varieties connotes a different physiological race whose identity in turn is fixed by this means.

Work of this nature, carried out in various countries, has resulted in the identification of about 150 physiological races of wheat stem rust, 10 of oat stem rust and 60 of wheat leaf rust.⁽⁴⁴⁾ It is clear that if results of such work are to be comparable, all steps in the procedure must be standardised. There is still much to be done in this direction if world results are to be of real value for comparative purposes. A good deal of evidence points to the fact that some of the races recorded at present as being different are really identical with others whose behaviour has been worked out under different environmental conditions. Purity of the differentials and maintenance of the proper environmental conditions during the development of the rust are prime essentials. But if the methods are standardised, the determination of physiological races can be made quite definite and precise.

A question of great importance is whether these physiological races retain their identity. Much work has been done to determine the point. It has been established that these races are constant entities. Mutation sometimes occurs in them, and there is the record by Roberts⁽³⁹⁾ of a race of *P. triticina* which appears to be unstable. But this is exceptional.

Specialisation in Relation to Breeding for Resistance.

It has sometimes been stated that determinations of physiological races in this way do not help the plant breeder who has to do with rust resistance in mature plants. The field is, of course, the final court of appeal in relation to disease resistance as well as to other crop characteristics. But it is clear that it would be extremely difficult to devise practicable methods for the accurate determination of physiological specialisation in the field. Apart from the time and space that would be required for growing the plants to maturity, the difficulties in the way of obtaining full control of the conditions for making the tests would seem to be insuperable.

Whatever method of determination is used, the fact is beyond dispute that the stem rust fungus of wheat is a complex of a number of entities. In breeding, or in any other work connected with a pathogen, it is essential to know just what entity is being dealt with. The accepted determination method—using seedlings—allows a worker to identify his organism, and if his work be breeding for resistance, then he knows to what organisms his plant is resistant. By reason of the fact that changes are known to take place from time to time in the physiological races present in a given region, it is imperative to know the extent of the resistance he has obtained.

There are many instances in which it has been reported that the resistance of a particular variety "broke down" in an altered environment. These are generally cases in which the real happening was that a different physiological race of the pathogen was present in the new environment, and the variety which was resistant to the first race was susceptible to this second one. The change was in the pathogen, not in the host, and was not due to environmental influences.

Again, if the race or races present in the area are known, breeding for resistance may be facilitated. Thus in the work in progress, stem rust of wheat generally is severe at Hawkesbury Agricultural College, although it may be slight in the wheat belt. At present when race 34 is the rust present in Australia, selections made for resistance at H.A. College will prove similarly resistant in the wheat belt. It is probably due to the fact that this race has been ubiquitous in Australia for such a number of seasons that a tendency has been shown in some quarters to decry specialisation studies.

For yet another reason these surveys of the races present are important. Where the resistance of the varieties to particular races is known, workers in other countries where these same races occur may call upon such varieties at once to contribute the resistance that they require.

There are, of course, many cases in which there is complete correlation between the results obtained from a study of seedling reactions and those observed in the field. For example, residues of material are still on hand of wheat differentials grown at H.A. College in 1924, i.e. prior to the advent of *P. gr. Tritici* 34. Races like 43 and 45 were those actually shown to be present in that area at the time. Straw of the varieties "Kanred" and "Kota" is

clean and quite free from rust attack, whilst that of "Einkorn" is black with rust. In those days it was only with the utmost difficulty that sufficient grain could be obtained from the latter wheat in order to retain it in the differential set. At the present time, owing to the presence of race 34, the difficulty is to get grain from the now heavily rusted "Kanred" and "Kota"; on the other hand "Einkorn" ripens perfectly free of rust. This is in complete agreement with the seedling behaviour of these wheats.

Again, in the years prior to the occurrence of race 34 in Australia, it was usual at an area like the Cowra Experiment Farm to find on varieties like "Canberra" and "Thew" mature leaves bearing a mixture of susceptible pustules and flecks. Cultures from these varieties, subjected to the ordinary determination treatment, revealed the presence of races like 43 and 45, and these in turn on seedlings of the original host plants showed complete agreement with the field reactions.

There have been repeated examples of this same correlation in the case of varieties of oats showing differential resistance to *P. graminis Avenæ*. Thus certain oat varieties in the field at maturing stages have frequently shown both susceptible and resistant pustules of stem rust on the same leaves. Cultures derived from these two types of pustule, when used to inoculate seedlings of the original varieties, produce the expected susceptible and resistant reactions. Again, a rusted plant of "Richland" oats collected at Cowra in 1936 yielded cultures of *P. graminis Avenæ* 8. This race is characterised by the susceptible seedling reaction on "Richland" oats.

Levine and Smith⁽³⁰⁾ in a recent important paper report the results of extensive investigations dealing with the possible correlations between seedling and mature plant reactions. Using all ten known races of *P. graminis Avenæ* to inoculate a number of oat varieties, they found that in no case was a variety resistant or susceptible as a seedling or adult plant without a corresponding reaction in the other phase tested. They conclude that seedling reaction is a reliable index of reaction of adult plants to specific physiological races of oat stem rust.

Studies dealing with the leaf rusts of wheat, oats, and barley have given similar results.

Küderling⁽²⁸⁾ with *P. glumarum Tritici*, Murphy⁽³⁴⁾ working with *P. coronata* and Asuyama⁽⁵⁾ with *P. triticina*,

have recorded similar concordance between seedling reaction in the plant-house and field behaviour of the nature plant. Myers⁽³³⁾ in recent work with rust of flax showed that the same gene conditions immunity in the field and glasshouse.

The general interpretation would seem to be that this type of resistance is protoplasmic. Cells of such plants at all stages of development possess the desired quality of resistance.

In contrast with such cases there are others in which there is not the same clear correlation between seedling and mature plant reactions. So far back as 1914, Stakman⁽⁴¹⁾ called attention to the strong susceptibility of Iumillo and Einkorn wheats, in the seedling stage, to certain races of stem rust, and their extreme resistance in the mature stage in the field. Other workers have since observed cases in which there is also lack of correlation between seedling and mature plant reactions. Such have come to light in our own work. Thus the differential variety "Acme" gives a susceptible seedling reaction to race 34 under some conditions in the plant house, whilst it is resistant as a mature plant in the field. Other varieties behave in a similar way. It should be pointed out that such varieties usually show chlorotic—and often nerotic—areas around pustules on seedling leaves under certain plant house conditions. At least in part this difference between seedling and mature plant behaviour is to be explained on the basis of the development in the mature plant of structural (or morphological) resistance, a type of resistance which obviously cannot be present in a seedling.

Physiological Races Present in Australia and New Zealand.

Adopting the generally accepted methods of determining specialisation, nine races of wheat stem rust have been found in the investigations of Australian and New Zealand material which commenced in 1921 and are still in progress. Their identities are set out in Table 2.

It has been pointed out before and is again emphasised that one group of three races, viz. 43, 44 and 54 show many similarities, and a second group comprising races 45, 46 and 55 are also similar. Both groups differ greatly from each other and from the other races 11, 34 and 59.

For purposes of comparison the relative frequencies with which these races have occurred are shown in Table 3, together with their origin. They do not include a large number of determinations of material received from New Zealand in 1935, which are to be reported upon separately.

The distribution of these races over the period of years that has elapsed since the inception of the work is shown in Table 4.

The change in the rust flora commencing in the 1926 season is a striking feature in these determinations. It is interesting to notice that, in general, happenings in Australia and New Zealand are parallel. In view of the usual W. to E. air movement and such an observation as the deposition of dust from Australia upon snow of the Southern Alps of New Zealand, it is to be expected that transport of uredospores may also take place across the Tasman Sea.

Such a change is, of course, not unique. Where continuous determination work has been in progress over a period of years in other countries, similar changes in the races present have been recorded. It is just such a change in the causal organism which complicates the work of breeding for disease resistance and makes necessary the continuous determinations of the races that are present in the locality concerned.

The origin of the race 34 in this case is difficult to explain. In other cases where barberries are regularly infected, the appearance of new races can readily be accounted for. The occurrence of race 11 in New South Wales in the 1935 season has been fully accounted for on this basis, since natural infections of barberries with race 34 had been found in 1933, and race 34 is known to be heterozygous and to produce race 11 as one of its segregates. But the appearance of race 34 in 1926 cannot be satisfactorily explained at the present time.

That it has had a profound influence upon our rust problem cannot be doubted. Apart from extended host range, in cultural studies under controlled conditions it is very striking to find how very rapidly new uredosori of race 34 are produced in comparison with the time taken for such races as 43 and 45. Field evidence indicates that rust damage in varieties which formerly were not severely attacked has become severe in recent times.

TABLE 2.
Typical Reactions of the naturally-occurring Physiological Races of Puccinia graminis Tritici in Australia and New Zealand.

Type of Reaction on Differential Wheat Variety.

Physiological Race.	Little Club C.I. 4066.	Marquis C.I. 3641.	Kanred C.I. 5146.	Kota. C.I. 5278.	Ar- nautka C.I. 4072.	Mindum C.I. 5296.	Spel- mars C.I. 6236.	Ku- banka C.I. 2094.	Acne C.I. 5284.	Ein- korn C.I. 2433.	Vernal Emmer C.I. 3686.	Khapli C.I. 4013.
11	4	4	3++	3++	4	4	4	3+++	3++	3	0;	1=
34	4	4	3++	3++	4	4	4	3+++	3++	1=	0;	1=
43	4	3++	0	0;	0;	0;	0;	×	1	3	1	0;
44	4	3++	0	0;	0;	0;	0;	3+	3+	3	1	0;
45	4	2	0	2-	4	4	4	×	×	3	3	1
46	4	3++	0	2-	4	4	4	1	1	3	3	1
54	4	3++	0	0;	0;	0;	0;	1	3	3	1	0;
55	4	4	0	2-	4	4	4	×	×	3	3	1
59	4	2	0	0	1	1	1	×	3	3	1	0

TABLE 3.
Summary of the Number of Isolations of P. graminis Tritici grouped according to their Origin.

Physiological Race.	Origin of Material.									Totals.
	A.C.T.	N.S.W.	Vict.	Qland.	S. Aust.	W. Aust.	Tas.	N.Z.		
11	2	14	—	—	—	—	—	1	17	
34	63	1,381	118	88	105	49	32	67	1,903	
43	—	130	7	17	3	2	1	—	160	
44	—	39	—	4	2	—	1	—	46	
45	1	33	3	—	7	—	2	3	49	
46	—	43	4	3	1	—	9	2	62	
54	—	4	—	—	1	—	—	—	5	
55	—	9	—	1	—	—	—	—	10	
59	—	—	—	1	—	—	—	—	1	
Totals ..	66	1,653	132	114	119	51	45	73	2,253	

TABLE 4.
Summary of the Number of Isolations of the naturally-occurring Physiological Races of P. graminis Tritici in Australia and New Zealand in the various years.

Physiological Race.	Season of Isolation ending 31st March of the year stated.														Totals.			
	1922	1923	1924	1925	1926	1927	1928	1929	1930	1931	1932	1933	1934	1935		1936	1937	1938*
11	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	17
34	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1,903
43	20	10	10	55	15	18	152	156	90	181	139	143	93	220	189	304	214	160
44	2	4	—	1	3	14	21	—	—	—	10	1	—	4	—	—	—	46
45	3	—	—	15	5	30	6	—	—	—	—	—	—	—	—	—	—	49
46	14	—	15	24	1	17	5	—	—	—	—	—	—	—	4	—	—	62
54	—	1	—	—	—	6	2	—	—	—	—	—	—	—	—	—	—	5
55	2	—	—	5	—	1	1	—	—	—	—	—	—	—	—	—	—	10
59	—	—	—	—	—	—	—	—	—	—	—	—	—	—	1	—	—	1
Totals	41	15	25	100	28	89	189	156	90	181	149	144	93	227	199	306	221	2,253

* The record for 1938 extends only to 1st January.

Varietal Resistance to Known Physiological Races.

In the early stages of the work when only these six races were known, extensive varietal tests were made with them. It is of value to set out these results which were obtained while these particular races were present in our crops.

This shows that the varieties tested fall into fourteen groups. The groups are set out in order depending upon the reactions exhibited by the varieties to the six races of rust. The latter are not arranged in their numerical sequence. It has been pointed out previously that there are affinities between races 43, 44, and 54 and also between races 45, 46, and 55, as determined by their behaviour on the differentials, so this arrangement of the races has been adopted here. This arrangement is further justified by the groupings set out below.

Group 1.

Varieties susceptible to all six races, giving the following results :

Race ..	43	44	54	45	46	55
Reaction	S.	S.	S.	S.	S.	S.

A 88, Akagomughi, Alaska Branched, Allies, Alpha, American Club, American 8, Autel White, Bald Knob, Baldry, Bandon, Barooga, Baroota Wonder, Bathurst 7, Bathurst 9, Bathurst 10, Bayah, Bearded Gluyas, Biffen's 60/29, Billy Hughes, Black Beardless Emmer, Black Winter Emmer, Blue Wave, Boonoo, Booran, Braemar Velvet, Cadia, Cairo 1, Cairo 2, Californian Club, Canimbla, Carinda, Cawnpur 13, Ceres, Chilian, Chinese White, Club E.A.S., Clubhead, College Purple, Comara, Comeback, Coreen, Correll's 8, Cowra 28, Cowra 31, Cowra 36, Cowra 39, Cowra 42, Cuballing, Cunana, Currawa, Dart's Imperial, Dauno III, Defiance, Early Defiance, Einkorn, Emperor, Etawah, Farmer's Friend, Federation, Fenman, Forelock, From Texas 3015-106, Fulcaster, Fultz, Gallipoli, Géant de Milanais, Glen Innes 2, Golden Drop, Gresley, Gwalior C 14, Hard Federation, Hatif Inversable, Hoof's Imperial, Hudson's Early Purple Straw, Hurst's 9, Improved Steinwedel, Indian 12, Indian 24, Indian F, Indian F × Telford's, Indian Dwarf Beardless, Indian Dwarf Semi-bearded, Indian Dwarf C.I. 4534, Indiana Swamp, Japanese 108, Japan Bearded, Japan Bearded U.S.A., John Brown, Jonathan, Jones' Fife, King's Early, King's Red, King's White, Little Club, Little Joss, Lott's White, Lotz, Mac's

White, Maharajah, Majestic, Major, Mammoth Amber, Martin Amber, Masolino, Mesopotamia T 45, Mesopotamia T 54, Minister, Nandero, Nangeenan, Narrogin, Narrogin 8, Newman's Early, Niloc, Nungarin, No. 6, No. 24, No. 76, No. 137, Ojirua, Onas, Peace Hybrid, Penny, Polish (England), Polish (U.S.A.), Polish (Short Glumes), Poole, Punjab 8 A, Punjab 11, Pusa 4, Pusa 6, Pusa 107, Quality, Radilla, Rajah, Rattling Jack, Red May, Red Rock, Red Wave, Red Wing, Ruby, Russian C.I. 4453, Russian C.I. 4454, Russian C.I. 4455, Russian C.I. 4456, Russian C.I. 4457, Russian C.I. 4459, Russian C.I. 4460, Russian C.I. 4462, Russian C.I. 4463, Russian C.I. 4464, Russian C.I. 4465, Rymer, Salt Wheat, Sands, Sanger's Prolific, Solid Straw Tuscan, Sonora, Spelt C.I. 3039, Stanley Brown, Stanley White, Steinwedel, Sun \times Dawson, Sunset, Synthetic Wild, Talgai, Tregorco Mendel, *Triticum orientale ensigne*, True Wild, Turvey, Union, Union 17, Union 28, Vac, Wallace, Waratah, Warden, White Federation, White Fife, White Odessa, White Tuscan, Wickepin, Wilfred, Wilhelmina, Yandilla, Yeoman C., Zaff, Zealand, Zealand Blue.

Group 2.

Varieties resistant to three and susceptible to three races as follows :

Race	..	43	44	54	45	46	55
Reaction		R.	R.	R.	S.	S.	S.

Anvil, Barletta, Bena, Booral, Bunge, Cad, Cadet, Canberra, Caliph, College Eclipse, Cowra 40, Cowra 41, Droophead, Duri, Early Bird, Early May, Early Purple Straw, Early Red Chief, Ensign, Equator, Exquisite, Farrer's Durum, Forge, Fortune, Gluyas, Graham, Gullen, Hamell, Hurst's 3, Indian F. \times Federation, Italy \times Bobs, Italian Spring C 4413, Marshall's No. 3, Pinet, Power's Fife, President, Prize-taker, Purple Straw, Riverina, Roseworthy, Russian C 4461, Silver Baart, Spelt Black Bearded, Spelt White Beardless, Stanley \times Yandilla King, Sultan, Theiss, Triumph, Warrah, Yandilla King.

Group 3.

Varieties resistant to three and susceptible to three races as follows :

Race	..	43	44	54	45	46	55
Reaction		S.	S.	S.	R.	R.	R.

Basil, Binya, Bobs, Bobs \times Federation, Bonus, Dindiloa, Hornblende, Nevertire, Pusa 31, Pusa 45, Red Bobs, Thew.

Group 4.

Varieties resistant to only one of the six races as follows :

Race ..	43	44	54	45	46	55
Reaction	S.	S.	S.	R.	S.	S.

Bomen, Cedar, Fane, Firbank, Florence, Ford, Geeralying, Haynes' Blue Stem, Haywood's, Hornbill, Kitchener, Narrogin 9, No. 1, Nyngan 3, Plowman's No. 2, Plowman's No. 3, Polish E.A.S., Quantity, Red Fife, Redit, S.H.J., Wagga 13.

Group 5.

Varieties resistant to only one of the six races as follows :

Race ..	43	44	54	45	46	55
Reaction	R.	S.	S.	S.	S.	S.

Cargo, Cleveland, Cudgen, Red Russian, Yuna.

Group 6.

Varieties resistant to two of the six races as follows :

Race ..	43	44	54	45	46	55
Reaction	S.	S.	S.	R.	R.	S.

Bathurst, Blount's Lambrigg, Bobin, Bunyip, Carrabin, Cowra 38, Eden.

Group 7.

Varieties resistant to two of the six races as follows :

Race ..	43	44	54	45	46	55
Reaction	S.	S.	S.	R.	S.	R.

Cowra 29, Hurst's 11.

Group 8.

Variety resistant to two of the six races as follows :

Race ..	43	44	54	45	46	55
Reaction	R.	S.	S.	S.	R.	S.

Felix.

Group 9.

Variety resistant to three of the six races as follows :

Race ..	43	44	54	45	46	55
Reaction	R.	R.	S.	S.	R.	S.

Imperial Amber.

Group 10.

Varieties resistant to four of the six races as follows :

Race ..	43	44	54	45	46	55
Reaction	R.	R.	R.	R.	S.	S.

Aussie, Cowra 30, Queen Fan, Union 66.

Group 11.

Varieties resistant to four of the six races as follows :

Race ..	43	44	54	45	46	55
Reaction	R.	R.	R.	S.	R.	S.

Italian Spring C 4411, Wandilla.

Group 12.

Variety resistant to four of the six races as follows :

Race ..	43	44	54	45	46	55
Reaction	R.	S.	S.	R.	R.	R.

Turkey Red.

Group 13.

Varieties resistant to five of the six races as follows :

Race ..	43	44	54	45	46	55
Reaction	R.	R.	R.	R.	R.	S.

Canaan, Nabawa.

Group 14.

Varieties resistant to all six races as follows :

Race ..	43	44	54	45	46	55
Reaction	R.	R.	R.	R.	R.	R.

Abyssinian, Alberta Red, Barwang, Clarendon, Emma, Euston, Galgalos, Galgalos E.A.S., Gaza, Kanred, Kota, Kharkov, Maem, Mentana, P 762, P 1066, P 1068, Persian Black, Preston, Rieti, Warren.

By far the greatest number of varieties fall into the first group characterised by susceptibility to all six races. Then there are two large groups in which the behaviour to races 43, 44, and 54 is similar, as it is also to races 45, 46, and 55. These in turn are followed by groups of varieties with resistance to one or more of the races, ending with the group in which resistance is shown to all six races.

Such a method of grouping serves to show what the opportunities are of combining desired resistances by crossing. At the same time it indicates that a number of varieties other than those of the accepted differential set may be used in the determination of the rust races concerned.

When race 34 appeared, the same varieties were tested with it in a search for resistance to this rust.

Of them, the only ones to show resistance were the following :

Abyssinian, Alberta Red, Einkorn (two strains), Emma, Gaza, Italian Spring C 4413, Maem, Persian Black, Pinet, Russian C 4458, Spelt Black Bearded, Trigo Africano.

Several hundred other varieties have been tested subsequently with race 34. The resistant ones were the following :

About Fashi, Acme, *Ægilotrichum triuncialis durum*, Africano, Akathistiko, Akrona (2 strains), Aleppo, Alicante 4, Aziziah, Bansi × Khapli 568 (3 strains), Beladi (9 strains), Bianrollo, Covelle, Crete 9, Cyprus (4 strains), Damascus (3 strains), Doubbi, Duro 34, D.5, Egypt (23 strains), Fedweb (several strains), Greece (8 strains), Greek 10, Haurani, Heiti, Hofed (many strains), Hope, Hope × Marquis × Yaroslav, H44-24 × Marquis, Iraq 11, Italian durum C 3430, Italian Spring, Iumillo, Joppa, Joppa Stranger, Kambouriko, Kawvale, Kenya Crossbred (20 strains), Khapli (3 strains), Margerito, Mahon de Teumara, Malakoff, Marouani, Marquis × Emmer, Marquis × Emmer Beardless, Marquis × Kanred × Marquillo, Marquis × Vernal Emma 20 (6 strains), Marquillo (2 strains), Mindum, Morocco (4 strains), Nodak (2 strains), Navarre 18, Pacific, Palestine (4 strains), Palestine durum 2650, Pentad × Marquis (5 strains), Persian Black, Pinet, Poona (6 strains), Portugal (14 strains), Russian (9 strains), Russian hordeiforme (2 strains), Salonica 17, Seville 19, Sinai (4 strains), Solid Straw durum, *T. Timopheevi* (2 strains), *T. durum leucomelon*, Vernal Emmer × Iumillo (2 strains), Vernal Emmer × Marquis × No. 138 (2 strains), Webfed 1/1, Webster (4 strains).

It is notable that amongst the latter, very few are vulgare wheats. The group of vulgares obtained from Kenya by the N.S. Wales Department of Agriculture are the most valuable of them. In the absence of precise information regarding the pedigrees of these wheats, Macindoe⁽³²⁾ has suggested that durum wheats have been used in their breeding. There are many durums in the list which are fully resistant to race 34. Breeding work with some of these has shown that the transference of their resistance to vulgare types does not present any real difficulty.

Of the varieties resistant to race 34, none has any commercial value under rust epidemic conditions in Australia. But they give the needed starting point in the breeding of useful types for our conditions.

It is interesting to compare the rust situation as shown by the occurrence of the nine races recorded in Australia with that revealed by determinations of rusts present in Britain. This work has involved the use of teleutospores sent by Dr. Alan Smith, Mr. W. Buddin and others from British areas. In no case have uredospores survived the journey from England. Inoculations of barberries have yielded aecidial cultures which have been multiplied in the uredospore stage and then used in the determination work. It is obvious that some of the races thus determined may be segregates of other uredospore races which are themselves heterozygous. Nevertheless the British rusts are seen to be totally different from ours.

From work extending over several seasons, the following races have been determined, viz. 23, 24, 27, 33, 35, 51, 53, 69, 83, 109, 117, and 122. In addition, at least 4 other races which are not recorded in the latest list⁽⁴⁴⁾ have been determined.

Again, it may be pointed out that whereas *P. graminis Secalis* has not yet been found in Australia, aecidial cultures derived from teleutospores on *Agropyron repens* sent by Dr. Alan Smith from Rothamsted, England, showed that this rust was the cause of the attack. As determined on the usual differential varieties, it was race 3. But when inoculated on to rye plants which had been continuously inbred for eight generations in another investigation that is in progress, both "4" and "1" pustules were produced side by side on the same leaves of certain of the plants. Obviously two races were present on this basis, although each would normally be recorded as *P. graminis Secalis* 3.

In all the many determinations of the stem rust attacking rye collected in the various Australian States, *P. graminis Tritici* of one of the known races has been present. Our rye rust problem is clearly quite different from that in England.

2. Leaf Rust of Wheat.

For many years it has been emphasised that leaf rusts do much more damage than is generally realised.⁽⁵⁴⁾ Investigations have been in progress for some time dealing with the causal organism, *P. triticina*. In the specialisation studies in Australia, two races have been found. As pointed out elsewhere⁽⁵⁵⁾ they are not separable on the usually accepted set of differential varieties, but by using the variety "Thew" (a number of other Australian

varieties serve the same purpose) the two races may be sharply differentiated. On this basis they are designated races 16 and 26 by Stakman⁽⁴⁴⁾ in his series of 58 races. They have been called "Aust. 1" and "Aust. 2" respectively in previous writings.

The determinations of the races present were commenced in 1926, and the results obtained since then are summarised in the following tables, the first showing their distribution in time and the second their distribution in space.

It will be seen that the two races are widespread in both senses. There has been a good deal of evidence to indicate that race 16 occurs more frequently in the early part of the rust season than does race 26. From New Zealand material the same two races have been determined many times, but in addition to them, several other races have been found.

It is clear that any control programme must take both races into account. As was done in the case of stem rust, more than 600 varieties of wheat were tested with them. The results showed that by far the greatest number of wheats are susceptible to both races. Those resistant are arranged in groups as under, in which it will be seen that a number of varieties are resistant to race 16 only, only one to race 26 alone, and a number to both the races. Amongst the last-named, vulgare wheats are rare.

Group 1.

Resistant to *P. triticina* 16.

Alberta Red, Basil, Bonus, Damascus (3 strains), Egypt 44, Euston, Fulcaster, Fedweb (several strains), H44-24 × Marquis (2 strains), Hofed (several strains), Japanese Bearded, Joppa Stranger, Kenya Crossbred C 6041, Leon 4, Malta 4, Palestine 3, Pentad × Marquis C 5981, Persian Black (2 strains), Poona 808, Portugal (2 strains), Russian 60, Stanley Brown, Stanley × Yandilla King, Thew, Webster (4 strains).

Group 2.

Resistant to *P. triticina* 26.

Early May.

Group 3.

Resistant to *P. triticina* 16 and 26.

Africano, Aleppo 4, Alicante (2 strains), Aziziah, Beladi (8 strains), Chinese White (2 strains), Cyprus (2

TABLE 5.
*Summary of the Number of Isolations of the Physiological Races of P. triticina from Australia and New Zealand
 in the Various Years.*

Physi- ological Race.	Season of Isolation, ending 31st March of the year stated.												Totals.
	1927.	1928.	1929.	1930.	1931.	1932.	1933.	1934.	1935.	1936.	1937.	1938.*	
16	3	52	60	20	35	63	58	54	107	87	75	41	655
26	3	70	71	20	34	50	56	45	80	63	54	19	565
Totals . .	6	122	131	40	69	113	114	99	187	150	129	60	1,220

* The record for 1938 extends only up to 1st January.

TABLE 6.
Summary of the Number of Isolations of the Two Australian Physiological Races of P. triticina according to their Origin.

Physiological Race.	Origin of Material.									Totals.
	A.C.T.	N.S.W.	Vict.	Qland.	S. Aust.	W. Aust.	Tas.	N.Z.		
16	22	513	33	24	37	9	2	15	655	
26	11	460	25	15	38	5	1	10	565	
Totals ..	33	973	58	39	75	14	3	25	1,220	

strains), Damascus, Democrat (2 strains), Egypt (5 strains), Einkorn (2 strains), Gaza, H44-24 × Marquis (5 strains), Hope, Hofed (several strains), Italian Spring, Iumillo, Joppa, Kawvale (2 strains), Malakoff (2 strains), Mediterranean, Norka, Pentad × Marquis, Pinet (2 strains), Portugal (3 strains), Red May, Russian C 4461, Salonica 17, Salt Wheat, Spelt White Beardless, T. Timopheevi (2 strains), Tunis 24, Valencia 1.

3. Stem Rust of Oats.

Of the ten races of *P. graminis Avenæ* that are known,⁽⁴⁴⁾ six have been found in Australia. Their identities are set out in the table which follows. It has been pointed out elsewhere that certain of the host reactions are subject to considerable fluctuation, particularly with changing temperatures. For example, without adequate temperature control it becomes impossible to separate races 1 and 2, and also races 3 and 7. Hence these two pairs of races are grouped in later tables.

TABLE 7.

Typical Reactions of the Naturally-occurring Physiological Races of P. graminis Avenæ in Australia.

Physiological Race.	Type of Reaction on Oat Variety.		
	White Tartar.	Richland.	Joanette.
1	2	2—	1
2	2	2—	3+
3	4	2	1
6	4	4	3+
7	4	2—	3+
8	2	4	3+

The distribution of these races is shown in the following tables in regard to both time and space.

It is clear that the complex of races 1 and/or 2 is the most widespread. A striking feature relating to races 3 and/or 7 is that in general they do not show up early in the rust season. They characteristically attack the "side" oats, and most of these are late-maturing types. There

TABLE 8.
Summary of the Number of Isolations of the Physiological Races of P. graminis Avenæ from Australia and New Zealand in the various years.

Physiological Race.	Season of Isolation, ending 31st March of the year stated.													Totals.	
	1925	1926	1927	1928	1929	1930	1931	1932	1933	1934	1935	1936	1937		1938*
1 and/or	30	3	21	38	39	38	62	54	48	34	72	66	55	38	598
2	—	—	—	2	6	—	—	—	—	—	—	—	—	—	8
6	—	—	—	7	4	2	13	5	6	5	5	8	9	25	89
3 and/or	—	—	—	—	—	—	—	—	—	—	—	—	1	1	2
7	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
8	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Totals	30	3	21	47	49	40	75	59	54	39	77	74	65	64	697

* The record for 1938 extends only to 1st January.

TABLE 9.
Summary of the Number of Isolations of P. graminis Arvenæ grouped according to their Origin.

Physiological Race.	Origin of Material.								Totals.
	A.C.T.	N.S.W.	Vict.	Qland.	S. Aust.	W. Aust.	Tas.	N.Z.	
1 and/or 2	17	470	24	32	31	8	8	8	598
6	—	6	2	—	—	—	—	—	8
3 and/or 7	3	73	4	2	—	—	6	1	89
8	—	2	—	—	—	—	—	—	2
Totals ..	20	551	30	34	31	8	14	9	697

would seem to be an interesting connection here between the rust and the developmental phases in these oats. The other two races, viz. 6 and 8, have occurred but rarely. It is of interest to note that the latter has quite recently been found as one of the several races obtained from æcidia on a barberry produced by inoculating it with viable teleutospores on oat straw sent from England. This culture has a characteristic, noted in certain other British races, of producing teleutospores on seedling leaves very soon after the initial inoculation.

The behaviour of numerous varieties of oats when inoculated with particular races has been determined. In this work race 6 was lost before the varietal tests were completed, and this incomplete set of reactions has therefore not been incorporated in these records. The results are summarised by grouping the varieties according to their reactions to the several races.

Group 1.

Varieties susceptible to all 5 races, giving reactions as follows :

Race	1	2	3	7	8
Reaction ..	S.	S.	S.	S.	S.

Abundance, Algerian, Algerian Tartar, *Avena barbata*, *A. brevis* (two strains), *A. byzantina*, *A. fatua suburnifolia*, *A. nudibrevis*, *A. sterilis Ludoviciana*, *A. sterilis polystachya*, *A. strigosa*, *A. strigosa glabrescens*, *A. strigosa orcadensis*, *A. strigosa pilosa*, *A. Wiestii*, Banner, Belar, Black Danish, Black Mesdag, Black Tartar 3552, Buddha, Budgery, Burt's Early, Calcutta, Chinese Skinless, Custes, Dun, Fergusson Navarro, Forward, Fulghum (six strains), Gidgee, Glen Innes No. 1, Guyra, Haver III, Kanota (two strains), Kelsall's, Kherson, Kurri, Lachlan, Lee, Ligowa, Lubra, Lubra Selection, Markton (two strains), Mulga, Myall, Nortex, No. 8, No. 15, No. 33, No. 35, No. 61, O.A.C. 3, Palestine, Quandong, Red Rust Proof (three strains), Red Rust Proof × Scotch Potato, Ruakura, Scotch Grey, South African Skinless, Stakman's Oats, Stark's Hooimaker, Sunrise, Trisperma Cu 110-2, Victoria, Victory, Warrigal, White Giant, Wilga, Yarran.

Group 2.

Variety resistant to 1 of the 5 races as follows :

Race	1	2	3	7	8
Reaction ..	S.	S.	S.	S.	R.

Bimbi.

Group 3.

Variety resistant (at low temperatures) to 3 of the 5 races as follows :

Race	1	2	3	7	8
Reaction	R.	S.	R.	S.	R.

Joanette.

Group 4.

Varieties resistant to 3 of the 5 races as follows :

Race	1	2	3	7	8
Reaction	R.	R.	S.	S.	R.

Advocate, Abr. × Victory × Reid's (two strains), Barker's Tartarian, Birdwood, Bradley (two strains), Burdett, Green Mountain, Iogold (one strain), Lampton, Minn. II, 22-70, Minn. II, 22-132, Minn. II, 22-177, Minn. II, 22-178, Minn. II, 22-183, Minn. II, 22-219, Reid's, Sun × Reid's (two strains), Weston, White Russian, White Tartar (two strains).

Group 5.

Varieties resistant to 4 of the 5 races as follows :

Race	1	2	3	7	8
Reaction	R.	R.	R.	R.	S.

Minn. II 22-177 (one strain), Black Tartarian.

Group 6.

Varieties resistant to 4 of the 5 races as follows :

Race	1	2	3	7	8
Reaction	R.	R.	R.	R.	S.

Burke (two strains), Early Kherson, Iogold (one strain), Laggan, Richland.

4. Leaf Rust of Oats.

In our coastal areas particularly, this rust does much damage. Last season gave a striking example of devastation of oats by *P. coronata*, as well as by *P. graminis Avenae*.

Over a period of years it has been noticed that a particular leaf of an oat plant in the field may show both susceptible and resistant pustules of leaf rust on it. This has been frequent in our Sydney University experimental plot. Only in recent years has the accepted set of differential varieties been available, but already five races of the rust have been sorted out. It has been found that the host reactions are very liable to vary with fluctuations in the temperature at which the plants are maintained. Never-

theless races can be identified with certainty under standardised conditions. Those determined are as follows: 3, 6, 7, 40, 47.

It is not considered fair at this stage of the work to tabulate the distributions of the races. When more determinations in time and in space have been carried out, this will be done.

Many varieties have been tested, but the work is incomplete and no attempt is made at this juncture to group them. Suffice to say that a few are resistant to all the races. These include three strains of oats belonging to *Avena strigosa*, and therefore of little value in a crossing programme, together with the varieties "Victoria", "Bond", and "Klein 69B". These, of course, give a definite starting point in the breeding of resistant varieties suitable for our conditions.

5. Leaf Rust of Barley.

In addition to stem rust, caused by races of *P. graminis Tritici*, the leaf rust causal organism, *P. anomala*, has been isolated from many sources. With one exception, these isolates have not shown any differences in the tests that have been possible. The differential varieties used by German workers have not been obtainable, hence no comparisons with races recorded overseas have been possible. The exceptional case just mentioned has the interesting characteristic of producing the resistant "2" reaction on "Kinver" barley, the variety always used throughout this work for culturing isolates because of its extreme susceptibility. Further work with this unusual race will probably bring to light other differences, but at present it is clear that at least two races of the rust occur.

Numerous varietal tests have been made and a number of resistant varieties determined. Lack of space prevents a tabulation of them here.

6. Leaf Rust of Rye.

Rye is not of great importance in Australia, but the rusts attacking it have been investigated. The stem rust present has invariably been one or other of the established races of *P. graminis Tritici*. Two seasons ago the first evidence of specialisation in its leaf rust, *P. dispersa*, was found. On the leaves of plants in the field were many cases in which both susceptible and resistant pustules were present. A very few completely resistant plants were

also present. Cultures were obtained from both types of pustule, and appropriate host plants selected and selfed. The difficulty in determining accurately from differential varieties what the two rusts are arises from the habit of cross-pollination in rye. Selfing of the resistant selections and of other plants chosen has led to complete sterility being manifested in most cases. Nevertheless efforts are still being made to carry this work through to its completion. Tests with a number of fertile strains of rye that have been inbred for eight generations have not yet brought to light any resistant types, but as more work is done, varieties suitable as differentials may become available.

7. Grass Rusts.

Already it has been recorded⁽⁵⁵⁾ that certain grasses in Australia are important hosts of cereal rusts. *Hordeum murinum* and *Agropyron scabrum* are notable examples. From one collection of the former, both oat and wheat stem rusts have been isolated, and sometimes more than one race of each of these rusts have been present. There have been very numerous instances of one race only being present on the grass examined. Clearly such grasses are important in the cereal rust work.

But there are other grass rusts which are not able to infect cereals. Some of them are important, causing considerable damage to the grasses attacked. No intensive work on the specialisation of these rusts has yet been undertaken, but there have been clear indications that physiological races occur in some of them. Thus in the case of *Lolium perenne* there have been instances of strongly resistant plants occurring in fields where most plants have been susceptible, and yet other plants have shown both resistant and susceptible pustules of *P. coronata* on the same leaves. This gives evidence of the presence of at least two races of this rust in that locality. Observations in other grass rusts will probably show similar evidence of specialisation. In breeding programmes designed to lead to the production of rust resistant strains of grasses, therefore, specialisation will have to be taken into account.

CONCLUSION.

Time and space will not permit of a description and consideration here of the actual results obtained in the breeding work that has been undertaken. Many controlled

investigations have been made, using material from crosses between parents differing in their resistance to particular races of stem and leaf rusts of known identity. These apply to wheat, oats, barley, and rye. Results of considerable genetical interest have been forthcoming, as well as of practical importance through the production of resistant types of agronomic value.

Looking now to the future, from what has been set out it is apparent that specialisation is to be expected in each of the cereal rusts. And it must not be forgotten that changes in the physiological races present may be looked for as time goes on. Any breeding programme designed to give control of rust should take fully into account this phenomenon of specialisation. The occurrence of "mature plant resistance" does not rule out the need for this.

It is to be expected that further results of outstanding value will be forthcoming from wide crosses, involving not only interspecific but also intergeneric hybridization. Our own work involving such wide crosses is giving valuable results. The cytogeneticist can make contributions of the greatest value in this sphere of the work.

A much fuller coordination of effort on the part of workers in many lands seems to be needed. Even within a single country there have been many evidences of wastage that would have been avoided by a pooling of knowledge and material.

But above all it seems to me that we need very much more fundamental research into the many problems connected with this subject. A great deal more exact knowledge on basic matters is needed if we are to go ahead confidently in this work of gaining control through the breeding of resistant varieties. And to this end I believe that this Society is making a useful contribution, and will do so in even fuller measure in the future.

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THE STRUCTURE OF ORIGANENE.

PART II. ITS IDENTITY WITH α -THUJENE.

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In Part I of this series (*J. Proc. Roy. Soc. N.S.W.*, 1937, 71, 330) the isolation of origanene from *Eucalyptus dives* oil was described and the properties of a number of its derivatives recorded. It was concluded that the substance was probably a bicyclic terpene $C_{10}H_{16}$, with one double bond. These conclusions have been confirmed and origanene, purified as thoroughly as possible, has been identified as a mixture of *d* and *dl* α -thujene (I). The latter gives a characteristic nitrosochloride apparently identical with that isolated by Pickles (*J.C.S.*, 1908, 868) from origanene. The identity of the two nitrosochlorides was confirmed by a comparison of the properties of the nitrolbenzylamines and nitrolpiperidines derived from them (Part I).* The difference in physical constants of the terpenes themselves could be attributed to the presence of α -terpinene in Pickles' fraction. (Cf. Henry and Paget, *J.C.S.*, 1931, 25.)

The only other natural occurrence of α -thujene on record is in the oil from the oleo-resin of *Boswellia serrata* (Simonsen, *Ind. For. Rec.*, 1922, 9, 290), but it has been prepared by a number of workers from thujyl alcohol (Tschugaeff, *Ber.*, 33, 3120; 34, 2279; 45, 1297, etc.).

In the table below a comparison is given of the physical constants of the substances obtained by Tschugaeff and Fomin (*Ber.*, 45, 1297), Simonsen (*loc. cit.*), Pickles (*loc. cit.*) with those of the terpene from *Eucalyptus dives*.

* After the reading of this paper, authentic specimens of the nitrolbenzylamine and nitrolpiperidine derivatives from the origanene of *Cyprus origanum* oil were made available by the kindness of Dr. T. A. Henry. A comparison of these derivatives with the corresponding ones prepared from the *E. dives* terpene definitely establishes their identity.

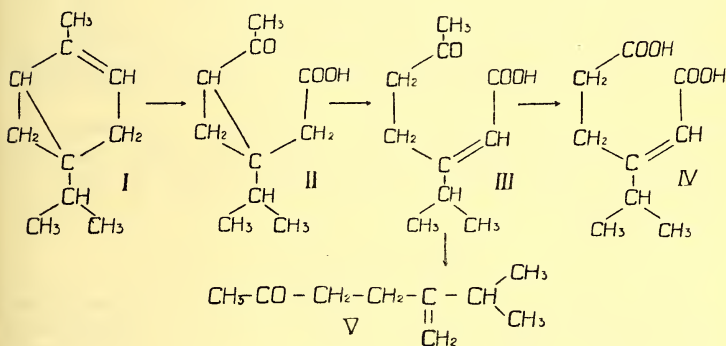
Tschugaeff.	Simonsen.	Pickles.	Terpene from <i>E. dives</i> .
B.p. 151°/759 mm.	B.p. 152°-152.5°	B.p. 160°-164°	B.p. 152°-153°
D ₄ ^{20°} 0.8301	D ₃₀ ^{30°} 0.8314	D ₄ ^{16°} 0.847	D ₄ ^{23°} 0.8330
n _D ^{20°} 1.4515	n _D ^{30°} 1.4502	n _D 1.480	n _D ^{24°} 1.4526
[α] _D -37°·2	[α] _D +37°·69 M _D 44.06	[α] _D +1°·50'	[α] _D +14°·5 M _D 44.1

The *E. dives* terpene was finally identified by a study of its oxidation products. Oxidation by means of aqueous permanganate solution has already been briefly described (Part I), only liquid products being isolated, but by the use of permanganate in acetone, much better results were obtained, possibly owing to the insolubility in acetone of the potassium salt of the acid formed. The liquid acid liberated from the potassium salt yielded on standing a small amount of crystalline material, which by its melting point (75°-76°) and its optical rotation ($[\alpha]_D -200^\circ$), seemed to be identical with α -thujaketonic acid (II), a sample of which, prepared by the oxidation of *d*-thujone, had a melting point of 75°-76°, and a rotation of +220°. A mixture of these two presumably enantiomorphous acids, as might be expected, melted at a considerably lower temperature. The liquid acid remaining after removal of the crystalline acid seemed to be mainly *dl* α -thujaketonic acid. Its specific rotation in aqueous solution was -40°, and it yielded a semicarbazone, m.p. 196°-197°, which gave no depression with the semicarbazones of either *d* or *l* α -thujaketonic acid, m.p. 197°-198°.

The crude acid also contained a small proportion of pinonic acid, since careful fractionation of the semicarbazone yielded a little *d*-pinonic acid semicarbazone, m.p. 205°, identified by comparison with an authentic specimen. From the appearance of this product it must be presumed that the original terpene contained some pinene.

On distillation under reduced pressure both the liquid and crystalline acids yielded another crystalline acid, which was undoubtedly β -thujaketonic acid (III). This was identified by comparison with an authentic specimen, by conversion to thujaketone (2-methyl-3-methyleneheptanone-6, IV), and by oxidation by means of sodium hypobromite to β -tanacetogen dicarboxylic acid (V).

There was thus no doubt of the identity of origanene and α -thujene, and this was further confirmed by the conversion of the dibromide to *p*-cymene by the action of pyridine and by the production of terpinene dihydrochloride by the action of hydrogen chloride in acetic acid (cf. Wallach, *Annalen*, 350, 167).



It will be observed that the optical rotation of the substance from *E. dives* was much lower than those recorded by Simonsen, and by Tschugaeff and Fomin, the low values recorded by previous authors probably being due to the presence of the highly dextro-rotatory β -thujene in the lævo α -thujene, rather than to the presence of *dl* α -thujene. The nitrosochloride, being inactive, is a derivative of *dl* α -thujene, and is not formed, at any rate readily, from the optically active substance. The failure of previous workers to obtain it is thus explained. The analogous difficulty of preparing pinene nitrosochloride from the optically active terpene is well known.

Eucalyptus dives oil is distilled commercially in very large quantities, so that a fraction consisting essentially of α -thujene is now available in large amounts.

EXPERIMENTAL.

Isolation.

This was carried out in the manner already described (Part I), the starting product being a low boiling fraction of *E. dives* oil kindly supplied by W. K. Burnside Pty. Ltd. of Melbourne, whose cooperation the authors gratefully acknowledge. This fraction contained some 40% of α -thujene, and 1,500 ml. finally yielded 500 ml. of pure substance. This had the physical constants already recorded in the table.

Catalytic Hydrogenation.

α -Thujene (8.5 g.) in alcohol (20 ml.) was hydrogenated in the presence of a palladium norite catalyst. Volume of hydrogen absorbed at 20° and 755 m.m., 1,700 ml.; calculated 1,550 ml. The product was a colourless oil, with a pleasant odour and having the following constants: b.p. 155°-160° C.; D_{22}^{24} 0.8177; $\alpha_D + 0^\circ.15$; n_D^{20} 1.4477; M_D 40.6 (calculated, 39.5). α -Thujane prepared by Tschugaeff and Fomin (*C.r.*, 1910, 151, 1058) had the constants: b.p. 157°/758 m.m., D_4^{20} 0.8139, $\alpha_D + 62^\circ.0$, n_D^{20} 1.4376.

 α -Thujene Nitrolamine.

This was prepared in a similar manner to α -pinene nitrolamine (Leach, *J.C.S.*, 1907, 1), and was obtained in good yield as large and beautifully formed prisms from alcohol, m.p. 162°. 0.0409 g. of the substance required 2.25 ml. of 0.958 N/10 hydrochloric acid for neutralisation, whence the equivalent weight is 184 (calculated for $C_{10}H_{16}NONH_2$, 182). On mixing with alcoholic hydrochloric acid it gave colourless needles of a hydrochloride, which after recrystallisation from alcohol melted with decomposition at 235° C., having previously darkened at about 200° C.

p-Cymene from α -Thujene Dibromide.

α -Thujene (10.8 g.) in acetic acid (40 ml.) was cooled in ice and bromine (12.7 g., 2 atoms) in acetic acid (20 ml.) slowly run in, with good stirring. The mixture was then poured into water (200 ml.), the heavy oil allowed to settle, separated, and added to pyridine (50 ml.). This mixture was refluxed for one hour, poured into dilute hydrochloric acid, extracted with ether and distilled.

The fraction boiling up to 180° (7 ml.) was shaken with a large volume of 5% potassium permanganate solution at 50° for 15 minutes, in order to remove unsaturated compounds, the mixture steam distilled, and the oil so obtained again distilled. Yield 5 ml., b.p. 174° - 176° , n_D 1.4900. This was undoubtedly *p*-cymene, since on oxidation by means of dilute nitric acid it yielded *p*-toluic acid (m.p. 177° C., mixed melting point with an authentic specimen 177° C.).

Production of Terpinene Dihydrochloride.

α -Thujene (5 ml.) was mixed with acetic acid (20 ml.) and dry hydrogen chloride passed into the solution until it was saturated. The dark red liquid was allowed to stand for twelve hours, and then poured on to ice. The crystalline material was drained on a porous tile, and recrystallised from methyl alcohol. Pearly plates, m.p. 51° C., mixed melting point with an authentic sample 51° C.

Oxidation of α -Thujene.

α -Thujene (40 ml., 33.2 g.) was added to acetone (500 ml.) (purified by distillation over potassium permanganate), the mixture stirred vigorously by means of a mechanical stirrer, and finely powdered potassium permanganate (90 g.) slowly dropped in over a period of five hours, the whole being cooled in ice so that the temperature did not rise above 6° C. The manganese dioxide sludge was filtered off and allowed to dry. The potassium salt of the acid was then extracted from the mixture by stirring with two successive lots of 200 ml. of water for thirty minutes. This extract was then acidified with concentrated hydrochloric acid, and extracted six times with 100 ml. of ether. The acid was removed from the ethereal solution by shaking with 100 ml. of 20% sodium hydroxide solution, which was then strongly acidified with hydrochloric acid, saturated with ammonium sulphate, and the oily acid collected by the addition of 50 c.c. of ether. After standing in a vacuum desiccator for twelve hours the crude acid was obtained as a pale yellow viscous oil. The object of this isolation process was to avoid heating the acid at any stage, and so prevent its isomerisation to β -thujaketonic acid. Yield, 35 g.

After thoroughly rubbing the crude acid with a little petroleum ether it was allowed to stand in the ice chest. After some hours a small amount of crystalline material

separated, and was filtered off. Recrystallisation from water yielded beautiful glistening plates, m.p. 75°-76° C. A saturated aqueous solution of this acid, obtained by allowing excess acid to crystallise on cooling a hot solution, had $\alpha_D -2^{\circ}\cdot87$ in a 5 cm. tube. Since 5 ml. of the solution required 6.2 ml. of 1.044 N/10 NaOH for neutralisation, it contained 2.38 g./100 ml., and $[\alpha]_D -200^{\circ}$. Thomson (*J.C.S.*, 97, 1510) gives $[\alpha]_D +244^{\circ}$.

The semicarbazone of the crystalline acid after recrystallisation from alcohol was obtained as colourless needles, m.p. 197.8° C., with decomposition, while the semicarbazone of the liquid acid, also obtained as crystalline needles from alcohol, was apparently less soluble and melted at 196.7° C. The mixed melting point was, however, 196.7° C. The equivalent weight of both substances was 241 (calculated for $C_{10}H_{16}O_2NNHCONH_2$, 241).

α -Thujaketonic Acid.

The crude product from an oxidation exactly similar to the last (33 g.) was distilled under reduced pressure. A small fraction was obtained boiling up to 159° C./2.25 m.m., and then the acid boiled constantly at 159°-161°/2.25 m.m. The first fraction was shown to consist essentially of thujaketone by the preparation of the characteristic semicarbazone, which crystallised in pearly plates from alcohol and melted at 141° C., the mixed melting point with an authentic sample being also 141° C. The second fraction rapidly solidified, and was rubbed with 20 ml. of petroleum ether (60°-80° C.) and filtered. Yield of crude crystalline acid, 27 g. This was recrystallised from water as silky needles, m.p. 78°-9° C. (15 g.). The acid was optically inactive.

0.6809 g. of the acid required 35.4 ml. of 1.044 N/10 NaOH for neutralisation, whence the equivalent weight is 184. (Calculated for $C_{10}H_{16}O_3$, 184.) The acid did not lower the melting point of β -thujaketonic acid prepared from thujone.

A semicarbazone was obtained as colourless needles from alcohol, m.p. 202°, undepressed by β -thujaketonic acid semicarbazone, m.p. 202° C.

0.6347 g. of semicarbazone required 25.4 ml. 1.044 N/10 NaOH for neutralisation, whence the equivalent weight is 240. (Calculated for $C_{10}H_{16}O_2N \cdot NHCONH_2$, 241.)

Found: C, 54.1%; H, 7.9%; calculated for $C_{10}H_{16}O_2NNHCONH_2$, C, 54.8%; H, 7.9%.

β -Tanacetogendicarboxylic Acid.

Bromine (1.4 ml.) was dissolved in a solution of caustic soda (3 g.) in water (50 ml.), and a solution of β -thujaketonic acid (1 g.) in dilute caustic soda added. Oily material began to separate at once, and after standing for an hour this was removed by ether extraction. It proved to be bromoform (b.p. $150^\circ C.$, carbylamine reaction) and carbon tetrabromide (m.p. $94^\circ C.$). A little sodium bisulphite was added to the aqueous solution in order to remove excess hypobromite, and it was then acidified, saturated with ammonium sulphate, and submitted to continuous ether extraction. The oil so obtained eventually solidified, was drained on a porous tile, and recrystallised from a mixture of ether and ligroin. It melted at $116^\circ-7^\circ C.$, the yield of recrystallised product being 0.7 g.

0.1683 g. required 16.8 ml. of 1.044 N/10 NaOH for neutralisation, whence the equivalent weight is 95 (calculated for $C_8H_{12}(COOH)_2$, 93).

Thujaketone.

β -Thujaketonic acid was distilled slowly at atmospheric pressure, and the oil so obtained washed with sodium carbonate solution and redistilled. B.p., $180^\circ-190^\circ$. It yielded a semicarbazone, m.p. 141° , mixed melting point with an authentic sample, $141^\circ C.$ The 2:4 dinitrophenylhydrazone (orange plates from alcohol) melted at $59^\circ C.$

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DETERMINATION OF ASCORBIC ACID IN THE
PRESENCE OF HÆMOGLOBIN.By RUDOLF LEMBERG, D.Phil.,¹and JOHN WILLIAMSON LEGGE, B.Sc.,²*Institute of Medical Research, Royal North Shore Hospital, Sydney.*

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It has been found that in solutions of oxyhæmoglobin ascorbic acid cannot be determined quantitatively by titration with 2·6-dichlorophenolindophenol or iodine after deproteinisation with acid reagents, e.g. $\text{CCl}_3 \cdot \text{CO}_2\text{H}$, HPO_3 . This loss is avoided if the oxyhæmoglobin is reduced to hæmoglobin before precipitation.

Two explanations have been advanced to account for this phenomenon. Gabbe (1937), Berend and Fischer (1937), and Fischer (1937) believe that oxyhæmoglobin adsorbs the vitamin while reduced hæmoglobin does not. Fischer claims that ascorbic acid can be washed free from the precipitated protein, and that H_2S -reduction of the protein-free filtrate does not recover any ascorbic acid. The precipitated protein, however, is not oxyhæmoglobin, but acid hæmatin-denatured protein, and, since the precipitations were not carried out under anærobic conditions, reduced hæmoglobin would also give the same product.

On the other hand, Van Eekelen (1936), Borsook *et al.* (1937), Johnson and Zilva (1937), and Emmerie and Van Eekelen (1937) support the view that not an adsorption but a reversible oxidation of the vitamin occurs when the proteins are precipitated. If this were so, subsequent reduction by H_2S of the dehydroascorbic acid in the filtrate should make possible the correct determination of ascorbic acid in a solution of oxyhæmoglobin. The difference between oxyhæmoglobin and reduced hæmoglobin is

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explained by the lack of oxygen necessary to oxidise the ascorbic acid [Emmerie and Van Eekelen (1937)].

It is, however, obscure, when this oxidation occurs. It has been reported that no apparent reaction takes place between oxyhæmoglobin and ascorbic acid, whether measured by the oxygen capacity of hæmoglobin or by the oxygen uptake in a manometer [Fischer (1937)]. Klødt (1936) believes that a reversible oxidation and reduction can take place between reduced hæmoglobin and dehydro-ascorbic acid. A more likely explanation is that the acid hæmatin-denatured protein plays a catalytic rôle in the oxidation of ascorbic acid, similar to that found by Lemberg, Cortis-Jones, and Norrie (1938) with acid hæmatin from pyridine hæmochromogen. Finally the oxygen liberated from the oxyhæmoglobin by the precipitating agents may oxidise the ascorbic acid.

EXPERIMENTS.

REACTION BETWEEN OXYHÆMOGLOBIN AND ASCORBIC ACID.

Fischer (1937) reports that at pH 6, no oxygen uptake occurs in a solution containing oxyhæmoglobin and ascorbic acid. We have found that in 10% Na_2HPO_4 , at pH 7.6 and 37° C. a reaction does take place, the oxyhæmoglobin being slowly reduced and afterwards broken down to bile pigment compounds (Lemberg, Legge and Lockwood, 1938) and the ascorbic acid oxidised. This oxidation of ascorbic acid is, however, a slow reaction, and has little to do with the instantaneous oxidation which occurs during the precipitation. In a solution containing 6 ml. of 10% hæmoglobin solution, 55 mg. ascorbic acid and 55 ml. 10% Na_2HPO_4 the following changes were observed in the concentration of reduced ascorbic acid. The solution was incubated at 37° C. and the ascorbic acid was determined by the method given below. Initially the ascorbic acid concentration of the solution was 0.90, after 5 minutes 0.79, after 25 minutes 0.56, after 160 minutes 0.23 mg. per ml. A further experiment was carried out in this way: 0.2 ml. oxalated sheep's blood was laked in 1.8 ml. water, 0.2 ml. ascorbic acid solution (0.3 mg.) was added; 1 ml. 30% HPO_3 was used as the precipitating agent. In one group of determinations oxyhæmoglobin was precipitated immediately, in another group the ascorbic acid and oxyhæmoglobin were allowed to stand for 30 minutes at room temperature before precipitation. No significant

increase of the loss of ascorbic acid (25% of the original concentration) was found in the second group. The large loss cannot, therefore, be explained by any reaction between oxyhæmoglobin and ascorbic acid before precipitation.

Has the acid hæmatin-denatured protein a catalytic effect on the ascorbic acid oxidation?

Here precipitation was carried out immediately after the ascorbic acid had been added to the oxyhæmoglobin, and the solution was allowed to stand in contact with the precipitate for varying lengths of time, to see if the acid hæmatin-denatured protein had any catalytic effect on the oxidation, subsequent to the precipitation. As a control the ascorbic acid was left standing in HPO_3 solution of the same strength. It was found that in 45 minutes a mean loss of 3% was observed in the HPO_3 solution. In the solution which contained the precipitate, the loss of 26% immediately after the precipitation had only increased to 30% in 30 minutes. The main loss is due to the oxidation during precipitation and the increase by about 4% of that loss in 30 minutes' contact with the precipitate, does not differ significantly from the increase in HPO_3 alone; this shows that the acid hæmatin-denatured protein does not possess any considerable catalytic powers.

Influence of the amount of oxyhæmoglobin.

The relative proportions of the reactants were varied, the amount of the precipitating reagent kept constant, and the loss of the ascorbic acid studied under these conditions. The ascorbic acid solution contained 2.1×10^{-3} mM. in 0.2 ml. (Table 1). All the precipitations were carried out in air and the filtration carried out immediately.

TABLE 1.

0.2 ml. of the Ascorbic Acid Added to Oxyhb. 10%, ml.	Ascorbic Acid Loss in mM $\times 10^{-3}$.	0.2 ml. Oxy-hæmoglobin 10% added to Ascorbic Acid, mM 10^{-3} .	Loss of Ascorbic Acid mM $\times 10^{-3}$.
0.1	0.44	1.05	0.53
0.2	0.71	2.1	0.56
0.3	0.97	3.15	0.71
0.4	1.31	4.2	0.66

It can be seen that with increase of the oxyhæmoglobin concentration the loss of the vitamin increases almost proportionally, while increasing the ascorbic acid concentration causes only a slightly greater loss of ascorbic acid.

H₂S-reduction of the filtrate and anaerobic precipitation.

In one experiment ascorbic acid equivalent to 1.29 ml. of indicator was added to a solution of laked erythrocytes which was precipitated after standing for 10 minutes in air, while in another experiment the hæmoglobin was reduced by a stream of CO₂ for 10 minutes before the precipitation. Equal volumes of the filtrates were reduced with H₂S overnight and the H₂S removed by bubbling nitrogen through the solutions. In this way the total amount of ascorbic acid was recovered, whether oxyhæmoglobin or reduced hæmoglobin had been present at the moment of precipitation (1.34 ml. indicator in the experiment with oxyhæmoglobin, 1.36 ml. in the experiment with reduced hæmoglobin). This shows that no removal of the ascorbic acid by adsorption to the precipitate takes place.

It was found more expedient as a method for the determination of ascorbic acid in presence of laked erythrocytes to reduce the oxyhæmoglobin by evacuation and use of oxygen-free nitrogen, than to reduce with a current of CO₂. The reduction was carried out in a Thunberg tube with the HPO₃ in the bent stopper.

With the difference that the hæmoglobin was reduced before precipitation, the experiments of Table 2 were carried out as those of Table 1.

TABLE 2.

0.2 ml. Ascorbic Acid added to Hb. 10%, ml.	Ascorbic Acid Loss mM × 10 ⁻³ .	0.2 ml. Hb. Solution 10% added to Ascorbic Acid, mM. × 10 ⁻³ .	Ascorbic Acid Loss mM × 10 ⁻³ .
0.1	0.19	—	—
0.2	0.13	2.1	0.0
0.3	0.17	3.15	0.1
0.4	0.22	4.2	0.45

A recovery between 90 and 100% of the added ascorbic acid is obtained, while from 40 to 80% only are recovered when the oxyhæmoglobin is precipitated in air. The small loss in the anaerobic experiments is probably due to

adsorption of ascorbic acid to the denatured protein precipitate.

In these experiments, as in those described above, the blank indicator titration of the filtrate from the reduced hæmoglobin was larger than the blank on the oxyhæmoglobin, which is explained by the presence of the reducible substances in the blood. If CO-hæmoglobin is used instead of oxyhæmoglobin, there is also no oxidation of ascorbic acid.

Oxygen evolution during the precipitation.

The amount of oxygen evolved by precipitation with HPO_3 from equal amounts of hæmoglobin in the absence and in the presence of ascorbic acid, was determined in a Van Slyke manometric apparatus by absorption of CO_2 by NaOH and of oxygen by $\text{Na}_2\text{S}_2\text{O}_4$ [Peters and Van Slyke (1932)]. The difference, expressed in milliatoms of oxygen, was compared with oxygen required for the oxidation of ascorbic acid to dehydroascorbic acid.

0.5 ml. hæmoglobin (11.35%) and 1.5 ml. H_2O precipitated with 0.3 ml. HPO_3 evolved an oxygen pressure of 72.5, 74.3 mm. mercury in a volume of 0.5 ml. gas. 0.5 ml. hæmoglobin, 1.0 ml. H_2O and 0.5 ml. ascorbic acid solution, precipitated with 0.3 ml. HPO_3 evolved an oxygen pressure of 53.8, 53.7 mm. mercury. Blank oxygen in solution 25 mm. mercury. Mean loss of oxygen 19.6 mm. mercury. This when converted to milliatoms equals 1.1×10^{-3} milliatoms oxygen. In a third set of experiments the precipitation of hæmoglobin in the presence of ascorbic acid was carried out in the same way in the chamber of the Van Slyke apparatus, but the liquid was expelled and the loss of ascorbic acid determined by indicator titration. 0.5 ml. of the ascorbic acid solution contained 1.86 ml. indicator; ascorbic acid recovered: 1.276, 1.171 ml. indicator. The loss of 0.584, 0.689 ml. indicator equivalents corresponds to a loss of 1.62, 1.92, $\times 10^{-3}$ mM. ascorbic acid.

The amount of ascorbic acid oxidised as calculated from the oxygen uptake is thus somewhat less than the loss apparent from the titration. One fact of interest from this experiment is the demonstration that in the metaphosphoric acid precipitation of oxyhæmoglobin under these conditions about 60% of the oxygen in the oxyhæmoglobin is not evolved. Since no more than 25% of the oxygen can be used up for the oxidation of the iron

in hæm, about 35% disappear in an unaccounted way, probably oxidising the protein moiety of the molecule.

The amount of ascorbic acid oxidised by a given amount of hæmoglobin when precipitated by HPO_3 under standard conditions is little influenced by temperature. Ascorbic acid equivalent to 1.22 ml. of indicator was used together with 0.2 ml. of oxyhæmoglobin (20%). At 4° C. ascorbic acid corresponding to 0.44 ml. of indicator was oxidised, at 18° 0.40 ml., and at 40° 0.23 ml.

DISCUSSION.

It is apparent that the rapid loss of ascorbic acid occurring in solutions containing oxyhæmoglobin during protein precipitation is due neither to a reaction with oxyhæmoglobin nor to an oxidation by molecular oxygen catalysed by the precipitate of acid hæmatin-denatured protein. It occurs during the liberation of oxygen by acidification, not however when the oxygen is set free by evacuation or by inert gases. The oxidation appears to have no temperature coefficient, which makes it probable that the oxidising agent does not require activation. Pauling and Coryell (1936) have shown that the oxygen in oxyhæmoglobin differs in electronic configuration from molecular oxygen, since the paramagnetism of the latter is lost in oxyhæmoglobin. It may be that it is this oxygen set free by the acid denaturation of the globin which oxidises the ascorbic acid.

SUMMARY.

1. When oxyhæmoglobin is precipitated by HPO_3 in the presence of ascorbic acid, the oxygen set free at the moment of precipitation is able to oxidise some of the ascorbic acid to dehydroascorbic acid.

2. This oxidation may be prevented by forming CO-hæmoglobin, or by reducing the oxyhæmoglobin and carrying out the precipitation under anærobic conditions.

3. A small amount of adsorption of ascorbic acid to denatured protein may take place in rather concentrated solutions, but this is only a small fraction, up to 10% of the total ascorbic acid oxidised.

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THE BILICHRYSINS. A NEW TYPE OF BILE
PIGMENT.

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We describe in this paper two compounds belonging to a new type of bile pigment, yellow in colour, differing from all known types of bile pigments. For these two pigments, arising respectively from biliverdin and mesobiliverdin by oxidation with two equivalents of iodine in the presence of zinc acetate, we suggest the names bilichrysin and mesobilichrysin. The analytical data of mesobilichrysin agree well with the formula $C_{33}H_{38}N_4O_7$, containing one atom of oxygen more than the formula of mesobiliverdin ($C_{33}H_{38}N_4O_6$). Probably this excess oxygen atom is present in the form of a carbonyl group linking two pyrrole rings and replacing a CH-group of mesobiliverdin.

There exists a close relationship between these pigments and the biliviols, the chrysin arising by isomerisation or hydration of unstable biliviols, and yielding again biliviols of another type by oxidation. Biliviols are bile pigments which are characterised by the following properties: The neutral colour is red to violet, the acid colour violet to blue-violet, the absorption spectra in acid aqueous solution show the strongest band in the yellow, a weaker band in the green, the zinc salts are blue to blue-green with red fluorescence and show a strong band in the orange and a weaker band in the green.

EXPERIMENTAL.

Preparation of Mesobilichrysin. N/10 alcoholic iodine solution is slowly added with shaking to a solution of 300 mg. mesobiliverdin and 200 mg. zinc acetate in 40 ml. methyl alcohol containing 0.2 ml. concentrated ammonia.

* Working under the T. E. Rofe Foundation.

After the addition of 5 ml. iodine solution, another 0.2 ml. concentrated ammonia is added and the addition of iodine solution is continued till the band of mesobiliverdin zinc at 685 $m\mu$ is entirely replaced by that of mesobiliviolin zinc at 622 $m\mu$. At this stage there has not yet appeared any trace of the band in the green of choletelin zinc, a product of the further oxidation of mesobiliviolin zinc. The total N/10 iodine solution used is 10.24 ml. (corresponding to 2.01 atoms iodine per molecule of bile pigment). The solution now shows an intense red fluorescence and is of pure blue colour. After pouring into chloroform the solution is washed with 2% acetic acid to remove all zinc salts and then washed till the washings are free from acid. The spectrum of the neutral solution now shows a single diffuse band at 554.5 $m\mu$. From a sample of the solution, 1% hydrochloric acid extracts the greater part of the pigment. We will call this unstable mesobiliviolin, mesobiliviolin II. The chloroform solution dried over sodium sulphate is allowed to stand overnight. During this time it has been largely converted into mesobilichrysin. The solution has assumed a brown-violet colour. Upon concentration of the chloroform solution yellow crystals of mesobilichrysin separate, leaving in solution a reddish violet violin, which can no longer be extracted from chloroform by 1% hydrochloric acid, and which in neutral solution shows two bands at 544 and 501 $m\mu$. This will be called mesobiliviolin III. The crystals are filtered off and washed with a minimum of chloroform. To recrystallise the yellow pigment, it is dissolved in pyridine, the pyridine solution diluted with water and poured into chloroform. The pigment remains in the aqueous layer. It is driven into chloroform by cautious addition of hydrochloric acid, with frequent shaking to prevent precipitation in the aqueous layer. The chloroform solution is extracted several times with 10% hydrochloric acid to remove pyridine and violin. The chloroform layer is washed till the washings are neutral, concentrated till crystals begin to separate, and then allowed to cool.

Yield, about 40 mg. after two recrystallisations.

An attempt was made to carry out the preparation in the absence of oxygen in order to see whether the transformation of the first-formed violin into mesobilichrysin is an isomerisation or an autoxidation. The iodine oxidation, the extraction by chloroform, and the washing of the chloroform were done as far as possible in an atmos-

phere of carbon dioxide, and the solution allowed to stand overnight under carbon dioxide. Mesobilichrysin was obtained in the same yield, while, to judge from the properties of the mesobilivolin in the solution standing overnight, very little mesobilivolin III had been formed. Mesobilichrysin is, therefore, an isomerisation product of mesobilivolin II and must contain two hydrogen atoms less or one oxygen atom more than mesobiliverdin.

The melting point of mesobilichrysin, when heated quickly, was found at 240° C. with decomposition. When heated slowly the pigment darkens, passing through brown to black from 170° to 215° and melts at 231° C.

Analyses (carried out by Dr. Weiler, Oxford, England).

Dried at 80° C. *in vacuo* there was no loss of weight.

4.132 mg. gave 9.790 mg. CO₂, 2.400 mg. H₂O, 0.021 mg. residue.

3.919 mg. gave 9.280 mg. CO₂, 2.290 mg. H₂O, 0.021 mg. residue.

3.130 mg. gave 0.247 cc. N₂ (756 mm. 20° C.).

The substance contains no chlorine.

	C.	H.	N.
Found (without allowing for residue)	64.62	6.45	9.15
	64.58	6.49	
Found (after allowing for residue) ..	64.95	6.49	9.20
	64.93	6.53	9.30
Calculated for C ₃₃ H ₃₈ N ₄ O ₇	65.76	6.36	9.30
C ₃₃ H ₃₆ N ₄ O ₆	67.79	6.20	9.58

Mesobilichrysin is easily soluble in pyridine, dissolves with difficulty in alcohol, chloroform, acetone, ethyl acetate, and ether, and is insoluble in petrol ether and in water. It is not extracted from a chloroform solution by 25% hydrochloric acid, but leaves chloroform to go into 50% sulphuric acid, from which it returns to the chloroform on dilution of the acid. From ether the pigment is extracted by 25% but not by 10% hydrochloric acid.

No band is discernible by means of the visual spectroscope in solutions of mesobilichrysin, but there is end absorption in the blue. Measurements with the ultra-violet spectrophotometer¹ reveal a band at 416 m μ in ammoniacal solution.

Zinc acetate added to an alcoholic solution of mesobilichrysin produces an immediate deepening of the colour. If the solution is kept *in vacuo*, no other change occurs.

¹ Observations of Dr. R. Lemberg and Mr. H. F. Holden.

As soon as air is admitted the solution begins to change, showing after a few minutes a strong red fluorescence and bands appear at $618\text{ m}\mu$ and $580\text{ m}\mu$, a typical violin zinc solution. If the violin is taken into chloroform, washed free from zinc and then from acid, the neutral solution shows absorption bands at $544\text{ m}\mu$ and $500\text{ m}\mu$. Mesobilichrysin is thus transformed by oxidation into mesobiliviolin III. In ammoniacal alcoholic solution, the addition of zinc acetate causes a red fluorescence to appear accompanied by the bands of biliviolin zinc, and the solution turns green, but the intensities of the fluorescence and of the absorption bands slowly weaken, and, over several different intermediate stages, the solution finally reaches a greenish yellow colour without any fluorescence and displaying only a band at $458.5\text{ m}\mu$.

If sodium amalgam is added to an alkaline solution of mesobilichrysin and the solution shaken for about two hours the yellow colour of the chrysin is destroyed. A leuco-compound may be extracted from the solution by chloroform after acidification with acetic acid. The compound is quickly oxidised in air and gives a urobilinoid pigment which shows an intense green fluorescence with zinc acetate, and the absorption spectrum displays a band in the blue-green. Mesobilinogen, the leuco-compound of bilirubin, shows the same behaviour.

Preparation of Bilichrysin. To a solution of 62 mg. biliverdin in 30 ml. methyl alcohol containing 50 mg. zinc acetate and 0.1 ml. concentrated ammonia 2.07 ml. N/10 alcoholic iodine solution are added slowly. The violin zinc solution is greenish blue and shows an intense red fluorescence. The violin is taken into chloroform and allowed to stand for three days. The pigments are extracted from chloroform by 1% sodium carbonate solution and brought into ether by acidification with tartaric acid. Ten per cent. hydrochloric acid removes the violins and leaves a yellow pigment in the ethereal layer. After washing with water the ether solution is concentrated and the residue is recrystallised from methanol. Yellow needles are obtained.

Zinc acetate added to a bilichrysin solution in air slowly produces a red fluorescence and the bands of biliviolin zinc appear, the stronger band being at $637.8\text{ m}\mu$. characteristic of protobiliviolins, showing that the vinyl groups have not been affected during the preparation.

TABLE I.

Reaction.	Rubins.	Dihydromesobilirubin.	Urobilinoid Pigments.	Chrysin.
Gmelin	Green, blue, violet, red, yellow.	Immediately red.	No alteration.	Dirty red-green, violet.
FeCl ₃	Green.	Red.	Violet or none.	Purple.
Ehrlich	None.	On long standing, violet.	None.	On long standing, brown.
Diazo	Red.	Violet with green-purple dichroism.	None.	Only very slowly a little violet colour.
Zinc test	None at first, later slowly violin zinc.	—	Green fluorescent zinc salts.	At first only deepening of colour, later violin zinc salts.
Spectrum.	450 m μ , in alkali 432 m μ .	—	Absorption band in the blue-green.	(Meso-) 416 m μ max. in ammonia.
Melting point	(Meso-) 300°-315° C.	278°-284° C.	—	240° C.

Differentiation from other Bile Pigments. Table I gives the result from some colour reactions as well as the absorption spectra and the melting points of the chrysin and other yellow bile pigments.

The chrysin may be distinguished from the urobilinoid pigments immediately by the absorption spectra and by the zinc reaction; from the rubin by the Gmelin and the diazo reactions; from dihydromesobilirubin by the diazo reaction; from hydroxylated as well as from non-hydroxylated dipyrromethenes by the zinc reaction (the former do not yield fluorescent zinc salts, the latter yield zinc salts somewhat similar to urobilinoid pigments).

SUMMARY.

Two new pigments are described, bilichrysin and mesobilichrysin, belonging to a new class of bile pigments. They arise by iodine oxidation of verdins in the presence of zinc acetate, and isomerisation of the violins first formed. Analyses of mesobilichrysin agree with the formula $C_{33}H_{38}N_4O_7$. The chrysin contain, therefore, one atom of oxygen more than the verdins (or one atom of oxygen more and two atoms of hydrogen less than the rubin).

The chrysin are closely related to the violins.

THE HEAVY MINERAL ASSEMBLAGES OF THE
UPPER COAL MEASURES AND THE UPPER
MARINE SERIES OF THE KAMILAROI
SYSTEM, NEW SOUTH WALES.

By ALMA G. CULEY, M.Sc.*

(With Plates I, II.)

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I. INTRODUCTION.

Underlying the rocks of the Triassic System in the central-eastern portion of New South Wales are strata forming a stratigraphical unit whose fossil contents show the Permian affinities of the upper beds and the Upper Carboniferous affinities of the lower beds. This unit, formerly called Permo-Carboniferous, has been designated by the late Sir Edgeworth David the Kamilaroi System.⁽¹⁷⁾

The examination of the heavy mineral content of some Kamilaroi sediments was undertaken subsequently to the examination of some of the sediments of the Narrabeen Series of the Triassic System. A chance examination of some Kamilaroi specimens from the Hunter River district

* The work recorded in this paper was carried out while the author was connected with the Department of Geology, University of Sydney.

showed heavy mineral assemblages similar to some from the northern Narrabeen sediments.⁽¹⁶⁾ It was thought, then, that further study of the Kamilaroi sediments might show whether the Narrabeen sediments were partly redistributed Kamilaroi sediments, and that such a study would probably point to the source rocks of both series of sediments.

Specimens have been collected from the Kamilaroi exposures from various localities lying in the zone fringing Narrabeen exposures. The aim has been rather to examine specimens from different localities than to concentrate on detailed stratigraphical examination from only a few localities. About fifty specimens from the Upper Coal Measures and about thirty from the Upper Marine Series have been examined. For some of these specimens, and for information on their locality, horizon and rock association, I wish to thank Mr. L. L. Waterhouse, B.E., Dr. G. D. Osborne, Miss Germaine Joplin, B.Sc., Ph.D., Mr. P. Game, B.Sc., Mr. M. D. Garretty, M.Sc., and Mr. J. Dulhunty, B.Sc.

I also wish gratefully to acknowledge Mr. Waterhouse's help and advice during the preparation of this paper, and information given by Mr. Dulhunty concerning the geological boundaries in the north-western portion of the area.

II. GENERAL GEOLOGY OF THE UPPER MARINE SERIES.

(Plate I.)

The Upper Marine sediments were deposited in a sea working over the land surface from near "Port Stephens, to beyond Murrurundi, westwards to near Dunedoo, and thence southwards to Bateman's Bay."^(17a)

(a) Northern District.

In the Hunter River district the Upper Marine Series has a thickness in places of 5,000 feet.^(18a) This thickness is divided into two by the Muree Beds, which have a maximum thickness of about 550 feet, and which separate the Mulbring Beds (Crinoidal Beds) above from the Branxton Beds below. The Branxton Beds have a thickness of about 3,000 feet, but are themselves divided by the Fenestella Beds which are exposed in the Branxton Railway cutting. The Fenestella Beds are approximately 1,150 feet above the top of the Greta Coal Measures.⁽²⁹⁾

(b) Western District.

The Upper Marine Series of the western district outcrops in the valley floors and slopes immediately to the west of the Main Dividing Range from the Hunter Valley on the north to the Kangaroo Valley on the south. They have a thickness up to a few hundred feet only. The basal beds are coarse and conglomeratic but give place to alternating shales, sandstones and conglomerates.

(c) Southern District.

The Upper Marine Series of the southern area outcrops between Wollongong and four miles north of Bateman's Bay, west to the Shoalhaven River, and it is limited to the north by the Robertson Tableland.

The southern series has been divided into five horizons,^(23a) namely (in descending order), (1) red tuffs and clay shales, (2) crinoidal shales, (3) Nowra grits, (4) Conjola conglomerates, and (5) Ulladulla tuffaceous mudstones and sandstones.

The red tuffs are confined to the area north of the Shoalhaven River, while the crinoidal shales are present in the Nowra district and do not extend far south. The Nowra grits outcrop over a large area and merge into the Conjola conglomerates in the Milton district. At Ulladulla the Ulladulla mudstones outcrop. Harper suggests an overlap in the sedimentation towards the southern extremity of the Series, such that the southern rocks are younger than the Nowra grits.

It is estimated by Harper that the thickness of this Series in the Nowra-Cambewarra district is 3,660 feet.^(23b) The thickness decreases fairly uniformly at the rate of about forty feet to the mile in a south-westerly direction, reaching minimum thicknesses on the southern and westerly margins. The thickness at the southern extremity is only about 60 feet.

Estimated individual thicknesses are: (1) red tuffs, 690 feet; (2) crinoidal shales, 720 feet; (3) Nowra grits, 250 feet; (4) Conjola conglomerates, 1,400 feet, probably the basal phase of the Nowra grits, being well developed near Conjola, eight miles north of Milton^(23b); (5) Ulladulla tuffaceous mudstones with maximum thickness less than 400 feet.⁽⁶⁾ The first three estimates were made in the Nowra district.

A correlation of the Nowra grits with the Muree Beds of the northern coalfield has been suggested by David.⁽²⁰⁾

In the south-westerly area of the Upper Marine rocks (Tallong-Marulan district) the sediments are very thin, but they thicken fairly rapidly to the north-east. The Upper Marine beds overlie, with a very uneven base and strong unconformity, rocks of Ordovician, Silurian, and possibly Devonian age, while some overlie the Glenrock granodiorite.

Due to the proximity of this area to the margin of the old shore-line there have been rapid changes in sedimentation as indicated by current-bedding and variation in grainsize of the rock. The sediments consist of conglomerate and sandstone, with a few shale lenses, which may be difficult to distinguish from Upper Coal Measure rocks. In some places, e.g. at Tallong, coal (apparently of drift origin) makes its appearance amongst the coarse sandstones, grits, etc. This was formerly regarded as belonging to the Upper Coal Measures.

The total thickness of the Upper Marine Series at Badgery's Track, about six miles S.S.E. from Tallong, is over 400 feet.⁽⁴⁰⁾

For list and details of the localities of the Upper Marine specimens examined, see Table 1.

III. GENERAL GEOLOGY OF THE UPPER COAL MEASURES.

(a) Northern District.

In the Hunter River district the deposition of the Tomago Series in a freshwater lake succeeded that of the Upper Marine Series. The Tomago Series varies in thickness from about 500 feet to 3,000 feet. The coal seams proved in it are, in descending order, Top Seam, Tomago Thick Seam, Tomago Thin Seam, Scotch Derry Seam, Rathluba Seam, and Morpeth Seam.

The Series is made up of sandstones, shales, some conglomerates and coal seams.

The freshwater beds formerly called the Dempsey Beds are now known to be part of the Tomago Series, the absence of workable coal being due to the tapering out of the Tomago seams.

Succeeding the Tomago Series are the Newcastle Coal-measures, with a thickness of from 1,400 feet to 1,500 feet. These measures are divided into two. The lower division includes, in descending order, the Burwood Seam, Nobby's Seam, Dirty Seam, Yard Seam, Borehole Seam and Sandgate Seams. There are six coal seams of importance

in the upper division, but no reference will be made to these in this paper.

(b) Western District.

The Western Coal-measures attain only from 200 to 500 feet in thickness,⁽¹²⁾ and represent only the equivalent of the Newcastle Coal-measures, the Tomago Series not being present in this area. The Marangaroo conglomerate horizon is regarded as the base of the Upper Coal Measures in this locality, while the upper limit is set by the Katoomba Seam, which may be the equivalent of the Wallarah Seam of the Hunter River Coal-measures and the Bulli Seam of the Southern Coal-measures.

The three important seams of the Western Coalfield are : (1) Lithgow Seam, associated with the Marangaroo conglomerate ; (2) Dirty Seam, which outcrops well near Ilford ; and (3) Top Seam or Katoomba Seam.

The sediments consist of conglomerates, sandstones and shales, and bands of very fine " cherty " tuffaceous material occur near the top of the Series, as at Mt. Victoria and Katoomba.

(c) Southern District.

The coal-measure outcrops of the Southern Coalfield occur in the valley of the Kangaroo River on the south, along the lower eastern slopes of the Illawarra Coastal Range, and on the coastal headlands between Bulli and Coalcliff. Immediately north of Coalcliff they dip under sea level.

At Bulli the coal-measures are probably 1,000 feet thick. They thin off to the south, so that at Wollongong there are 800 feet of coal-measures in the slopes of the coastal range, and on the south side of Cambewarra a thickness of only 40 feet is attained.^(23c)

There are seven coal seams in the Southern Coalfield, the relative positions at Mount Kembla (as type section) being as follows (descending order) : No. 1 or Bulli Coal Seam, 25 feet of strata, No. 2 or " Four Feet " Seam, 100 feet of strata, No. 3 or Dirty Seam, 40 feet of strata, No. 4 Seam, 80 feet of strata, No. 5 Seam, 30 feet of strata, No. 6 Seam, 180 feet of strata, No. 7 Seam. There are marked local variations from these measurements.

The Bulli Seam is the only one extensively worked. By the courtesy of Mr. O. G. Vickery, B.E., one was able to visit the Coalcliff Colliery and collect specimens in the

mine roads. Specimens were collected at one-tenth of a mile intervals in a road running due west on the level of the Bulli Seam. Several specimens were collected in a tunnel descending from the Bulli Seam to the "Four Feet" Seam.

Other Southern Coalfield sediments consist of sandstones, shales (mainly carbonaceous), tuffs and tuffaceous shales.

In the Tallong district the coal regarded by Woolnough as belonging to the Upper Coal Measures is now believed (see p. 78) to form part of the Upper Marine Series.

For list and details of the localities of the Upper Coal Measure specimens examined, see Table 2.

IV. METHOD OF PREPARATION AND EXAMINATION OF CONCENTRATES.

The method of examination employed was similar to that described in the previous paper.⁽¹⁶⁾

In the crushing and sieving process it was found advantageous to separate the very fine dusty fraction, which inevitably results from crushing, from the coarser material made up of fragments about the average grainsize of the rock. In the case of the coarser sandstones and grits three separate fractions were sometimes kept—the coarser grains, the average grains, and the fine dust. By thus grading the crushed material the panning was facilitated and improved. The final separation was made with bromoform in small evaporating dishes as previously described. The heavy mineral concentrate was then weighed and the approximate percentage of the heavy mineral content determined. Further separations of the concentrate were effected by means of a horseshoe magnet and an electro-magnet. Monobrombenzol was used to immerse the grains for microscopic examination, and on evaporation of the immersion liquid the grains were recovered. Permanent mounts were made of these, using the method described by Reed.⁽³¹⁾ This method has proved very satisfactory. The remaining grains were preserved in sample bottles.

V. METHOD OF PRESENTATION OF RESULTS.

In tabulating (Tables 1 and 2) the relative proportion of the constituents in the concentrates a different scheme was adopted from that suggested by Milner⁽²⁷⁾ and employed

by various petrographers. No definite percentage limits for his symbols are suggested by him, and the expression of results is "to a certain extent governed by the apportioning powers of the observer." One feels very hesitant in presenting a table on the samples examined in this work with divisions so finely drawn.

The difficulties with which one is confronted are: (1) the lack of uniformity of grain size in the concentrate, e.g. the concentrate may have in it comparatively large zircon and very minute anatase crystals. In counting the grains it is left to the judgment of the worker to estimate equivalent sizes of the grains in order to obtain the relative proportions. (2) The rock cement may contain a carbonate (perhaps iron-bearing calcite or siderite), or limonite, which may flood the concentrate. Boiling in hydrochloric acid is necessary to remove these for the convenient examination of the remainder of the concentrate, and, in the process of boiling, apatite and magnetite, if present in the concentrate, would be destroyed; proportions cannot then be accurately determined. However, if one is content with a broader division as adopted in this paper, a rough estimate of the abundance of destroyable minerals may sometimes be made by a careful survey of portion of the concentrate before boiling in hydrochloric acid. (3) Also, one realises that when panning some of the heavy grains are lost. Smithson⁽³⁶⁾ gives figures for his experiments showing the difference between a concentrate obtained by panning followed by bromoform separation and one obtained by using bromoform alone. The latter he considers to give an accurate result. He states that, "So long as a petrologist always employs the same procedure it is probably safe for him to compare his estimates one with another." Such a comparison may be confidently made provided the symbols used do not claim too high a degree of accuracy.

For these reasons one adopted the scheme used in the previous paper and again in this paper, and shown in Tables 1 and 2.

The use of fewer symbols makes it easier to obtain a mental picture of the concentrates.

One would not feel hesitant in using Milner's scheme in the examination of natural sand concentrates where there is a certain amount of natural sorting and equality of grain size, and where there are usually fewer composite grains in various stages of alteration.

VI. TABLE I.
Summary of Mineral Distribution, etc., in the Upper Marine Series.

Number of Specimen.	Locality, Notes on Occurrence, Type of Sediment.	Approx. percent. heavy minerals.	Garnet.	Magnetite.	Pyrites.	Picotite.	Anatase.	Rutile.	Xenotime.	Zircon.	Apatite.	Ilmenite.	Tourmaline.	Barytes.	Brookite.	Hornblende.	Monazite.
1	Mindaribba (4 mile N. of), railway cutting, fine grey tuffaceous sandstone	0-04		P	P	P	P	P	P	P			P		P		
2	Mindaribba (3 mile S. of), coarse tuffaceous sandstone	0-03		P	P	P	P	P	P	P			P		P		
3	Branxton, railway cutting W. station, below <i>Fenestella</i> Beds, greenish sandstone	0-02		S	C	C	C	S		A	?		P				
4	Branxton, railway cutting W. station, 4 chains W. specimen 3, below <i>Fenestella</i> Beds, greenish sandstone	0-02		S	C	C	P	S		A	P		P				
5	Branxton, just above <i>Fenestella</i> Beds, greenish sandstone	0-07		S	C	C	S	S		A	P		P				
6	Mt. Bocabie, western flank, few feet above basal beds, very fine sandstone	0-01		P		P	P	P		A			P				
7	Rylstone (3 miles from), on Rylstone-Cudjogong Road, fine white sandstone	0-01		P		P	P	P		A			P				
8	Rylstone (6 miles S. of), near base U.M. Series, fine banded sandstone.	0-04		S	P	P	P	P		A			P				
9	Clandulla (3½ miles S. of), near base U.M. Series, grit and sandstone.	0-02		S	P	P	P	P		A			P				
10	Bowenfels (4½ miles S. of), main Western Road, sandstone grading into grit	0-04				P	P	P		A			P				
11	Bowenfels (west of), grit, possibly Marangaroo horizon	—				P	P	P		A			P				
12	Gangerang Range, cliff N.E. end Mt. Koorie Kirra, about 20 feet above base U.M. Series, grit	0-02		C	S	P	P	P		A			P				
13	Kanangra Walls, from the Dancing Cave, about 50 feet above base U.M. Series, grit	0-01		S	?	C	S	S		A		S	P				
14	Yerranderie, N.E. face Far Peak, probably near junction U.M. Series and U.C.M., sandstone	0-02		S	P	S	S	S		A		P	P				

The following symbols and approximate percentages refer to the heavy mineral concentrates:
 A = very abundant (> 75%),
 a = abundant (> 45%, but < 75%),
 C = very common (> 25%, but < 45%),
 c = common (> 5%, but < 25%),
 r = rare (> 1%, but < 5%),
 p = present but proportions not determined.
 P = present but proportions not determined.
 * denotes the presence of purple zircon.
 U.C.M. = Upper Coal Measures.

TABLE I.—Continued.
 Summary of Mineral Distribution, etc., in the Upper Marine Series.—Continued.

Number of Specimen.	Locality, Notes on Occurrence, Type of Sediment.	Approx. heavy minerals.	Garnet.	Magnetite.	Pyrites.	Picotite.	Anatase.	Rutile.	Xenotime.	Zircon.	Apatite.	Ilmenite.	Tourmaline.	Barytes.	Brookite.	Hornblende.	Monazite.
15	Tallong, base of Twin Trig, fine white sandstone	0.06								a							
16	Kangaroo Valley, Hampden Bridge, white friable sandstone, Nowra grit	0.02								a							
17	Wollongong, cliff S. main beach, tuffaceous sandstone	—								p							
18	Wollongong, just S. main beach, grey sandstone	—								a							
19	Wollongong, S. rock platform, fine sandstone	—								a							
20	Nowra, S. side Shoalhaven Bridge, grit	0.01								a*							
21	Nowra, N. side Shoalhaven Bridge, grit	—								a*							
22	Parma Creek, 6 miles S. Nowra on Prince's Highway, coarse sandstone	0.05								A*							
23	Nowra (11½ miles S. of), Prince's Highway, fine white shaly sandstone, <i>Strophalosia</i> numerous	—								A*							
24	Huskisson, Jervis Bay, glendonite horizon, fine grey sandstone	0.02	s							a*							
25	Milton (13 miles N. of), Prince's Highway, coarse sandstone	0.02								A							
26	Milton (11 miles N. of), Prince's Highway, fine white sandstone	0.19								a							
27	Conjola, 8 miles N. Milton, Prince's Highway, <i>Cheonomya</i> Beds, white sandstone	—								a							
28	Milton (6 miles N. of), Prince's Highway, fine banded sandstone	0.20								A*							
29	Ulladulla, Warden Head, Ulladulla mudstone	0.02								a*							
30	Ulladulla, Warden Head, dark grey sandstone	0.02	s							A							
31	Terrell, Prince's Highway, fine white sandstone	0.04	s							a							
		0.02								a*							

The following symbols and approximate percentages refer to the heavy mineral concentrates:

A = very abundant (>75%).

C = very common (>25%, but <45%).

r = rare (>1%, but <5%).

p = present but proportions not determined.

U.M. = Upper Marine.

a = abundant (>45%, but <75%).

c = common (>5%, but <25%).

s = scarce (<1%).

* denotes the presence of purple zircon.

U.C.M. = Upper Coal Measures.

Number of Specimen.	Locality Notes on Occurrence, Type of Sediment.	Approx. percent. heavy minerals.	Garnet.	Magnetite.	Pyrites.	Plectite.	Anatase.	Rutile.	Zircon.	Apatite.	Ilmenite.	Tourmaline.	Barytes.	Brookite.	Hornblende.	Monazite.
32	Brunkerville (1½ miles S. of), about 250-300 feet above base Newcastle Stage, fine white sandstone	0-03	s	c	c	c	c	s	a			s	p			s
33	Catherine Hill Bay (1¼ miles S. of), about 350 feet from top U.C.M., coarse white sandstone	0-02	s	r	c	r	r	r	a	p		c	p			s
34	Swansea (7-8 miles S. of), coarse sandstone and conglomerate	0-01		s	p	p	p	p	p			p				p
35	Swansea (5-2 miles S. of), coarse white sandstone	<0-01		s	r	r	r	r	a	s		r				
36	Swansea (8 miles N. of), friable white sandstone	0-02		s	r	c	s	s	a			r				
37	Newcastle, S. end Shepherd's Hill, about 5 feet above Yard Seam fine grey sandstone	0-02	r	s	c	r	s	a	r			c		s		
38	Newcastle, road cutting near obelisk, 5 feet below Burwood Seam, white sandstone	0-02			s	c	s	A				s				
39	Newcastle, N. end Shepherd's Hill, about 10 feet below Yard Seam, fine grey sandstone	0-02	s		c	r	a	s	a	c		r			s	
40	Tarro (3-3 miles W.N.W.), friable white sandstone	0-01		s	r	a	s	a				r				
41	Tarro (6 miles W.N.W.), light coloured grit	0-08	s		r	c	s	A				r				
42	East Maitland, Baker's Quarry, above Lower Rathluba Seam, white sandstone	—			s	r	a	s	a			r				
43	East Maitland, Baker's Quarry, just above Lower Rathluba Seam, grey sandstone	0-02	r		c				A	c		r				
44	East Maitland, Baker's Quarry, just below Lower Rathluba Seam, grey sandstone	0-01	r		c				A	c		r				
45	Singleton (3-2 miles N.W.), fine sandstone	0-02			p	p	p	p	p	a		p				
46	Broke (2-2 miles N. of), fine light coloured sandstone	0-02			r	c	c	s	a	a		r				
47	Denman, on Singleton-Denman Road, fine sandstone	0-12	r	s	c	c	s	a	a	c		r				
48	Wollar (19 miles E. of), Murrumbidgee Road, tuff	0-07	s	s	s	s	s	a	a	a		p				
49	Wollar (12 miles E. of), Goulburn River, fine tuffaceous sandstone	0-02	r	p	d	p	p	p	p	p		p				
50	Wollar (4 miles E. of), associated with <i>Glossopferis</i> -bearing shales, tuff	—			s	s	s	s	a	c		s				
51	Mt. Boodle (western flank of), about ¼ mile E. of No. 6 and 160 feet above it, fine brown sandstone	0-04			r	c	c	a				c				
52	Ilford (¼ mile S. of), near top U.C.M., fine white sandstone	0-01			r	r	s	A				r				
53	Clandulla, grey sandstone	0-02			r	r	r	r	A			r				
54	Capertee Hill (1-8 miles S. Capertee) associated with "cherts", fine white sandstone	—			?	r	c	A				r				
55	Ben Bullen (W. side railway line), near base U.C.M., grit	0-01	s	s	?	c	c	C	C			r				
56	Ben Bullen (E. side railway line), near base U.C.M., grit	0-01	s	s	?	c	c	C	C			r				

The following symbols and approximate percentages refer to the heavy mineral concentrates:

A = very abundant (> 75%),

C = very common (> 25%),

r = rare (> 1%, but < 5%),

p = present, but proportions not determined.

s = scarce (< 1%),

c = common (> 5%, but < 25%),

a = abundant (> 45%, but < 75%),

s = scarce (< 1%),

* denotes the presence of purple zircon.

HEAVY MINERAL ASSEMBLAGES.

Number of Specimen.	Locality, Notes on Occurrence, Type of Sediment.	Approx. heavy minerals.	Garnet.	Magnetite.	Pyrites.	Piccolite.	Anatase.	Rutile.	Zircon.	Apatite.	Ilmenite.	Tourmaline.	Barytes.	Brookite.	Hornblende.	Monazite.
57	Wallerawang, junction Bathurst and Mudjee Roads, grit sandstone	0-01						a	r	a*	r					
58	Mt. Victoria, main Western Road, near "chert" quarry, fine white sandstone	0-01						r	s	A	r			s		
59	Mt. Victoria, associated with "cherts" and shales, very fine white sandstone	0-01						c	s	A	s					
60	Katoomba, about 40 feet above "cherts", Federal Pass, brown shale.	0-01						c	r	A	s					
61	Tallong, ½ mile E. railway station on Wingello Road, coarse sandstone.	0-02						r	r	A	r					
62	Murrumba, main Southern Road, about 20 feet from top U.C.M., fine sandstone	0-06						r	c	r	c					
63	Warrima (1½ miles E. Tallong), coarse bedded sandstone	0-09						s	c	C	s					
64	Barrangarry Mt., fine "cherty", sediment	—						c	c	C	s					
65	Bull Point, about 500 feet below Bulli Seam, green tuff	0-03						c	c	C	c					
66	Thirroul, quarry of Vulcan Refractory Brick Co., about level of No. 6 seam, cream sandstone	—						r	s	r	a					
67	Thirroul, quarry of Vulcan Refractory Brick Co., about level of No. 6 seam, carbonaceous sandstone	—						r	r	A	c					
68	Austimmer, headland N. beach, about 15 feet below No. 5 seam, grey shaly sandstone	0-05						a	s	C	c					
69	Coledale, headland S. beach, about 20 feet below No. 5 seam, grey shaly sandstone	0-03						a	s	c	c					
70	Scarborough, between Coalcliff and Scarborough, near top U.C.M., grey sandstone	0-04						a	s	c	c					
71	Scarborough, about 115 feet below Bulli Seam, grey sandstone.	0-02						c	c	C	c					
72	Scarborough, about 20 feet below Bulli Seam, weathered sandstone	0-02						c	c	C	c					
73	Coalcliff, 0-1 mile W. Colliery main shaft, roof Bulli Seam, grey sandstone	0-02						a	r	C	c					
74	Coalcliff, 0-2 mile W. Colliery shaft, roof Bulli Seam, grey sandstone.	0-02						a	r	C	c					
75	Coalcliff, 0-25 mile W. Colliery shaft, roof Bulli Seam, grey sandstone.	0-02						a	r	C*	c					
76	Coalcliff, 0-35 mile W. Colliery shaft, roof Bulli Seam, dark grey sandstone	0-03						c	a	s	c					
77	Coalcliff, Colliery, roof "Four Feet", Seam, friable grey sandstone	—						a	r	C	c					
78	Coalcliff, Colliery, 5 feet above "Four Feet", Seam, grey sandstone	0-01						C	r	a*	c					
79	Coalcliff, Colliery, 10 feet above "Four Feet", Seam, fine grey sandstone	0-01						C	r	a*	c					
80	Coalcliff, Colliery, 15 feet above "Four Feet", Seam, grey sandstone with carbonaceous laminae	0-01						C	r	a	c					
81	Coalcliff, immediately below Bulli Seam, coarse grey sandstone	0-02						C	r	s	a	c	s	r		

The following symbols and approximate percentages refer to the heavy mineral concentrates :
 A = very abundant (>75%).
 a = abundant (>45%, but <75%).
 C = very common (>25%, but <45%).
 c = common (>5%, but <25%).
 r = rare (>1%, but <5%).
 p = present, but proportions not determined.
 U.M. = Upper Marine.
 U.C.M. = Upper Coal Measures.
 * denotes the presence of purple zircon.

¹ *Corrigenda.*—These specimens are now regarded as belonging to the Upper Marine Series.

VIII. DESCRIPTION AND DISTRIBUTION OF THE HEAVY MINERALS. (See Tables 1 and 2 and Plate II.)

The heavy minerals identified in the specimens examined from the Upper Coal Measures and the Upper Marine Series are :

<i>Cubic.</i>	<i>Tetragonal.</i>	<i>Hexagonal.</i>	<i>Rhombic.</i>
Garnet	Anatase	Apatite	Barytes
Magnetite	Rutile	Ilmenite	Brookite
Picotite	Xenotime	Siderite	
Pyrites	Zircon	Tourmaline	
		<i>Monoclinic.</i>	
		Hornblende	
		Monazite.	

In addition leucoxene, limonite, and hæmatite frequently occur. There is very little fresh ilmenite, but the leucoxene and much of the limonite, anatase, and secondary rutile are derived from ilmenite.

Garnet was identified in specimens from the northern outcrops of both Upper Coal Measures and Upper Marine Series. It was also present in the Western Coal-measures from Ben Bullen and in Upper Marine material from Wollongong, 11½ miles south of Nowra and Ulladulla in the southern area. It is a rare or scarce constituent when present. The grains are usually very irregular and show rough surfaces due to the dodecahedral cleavage. Cleavage plates are common in a sample from near Denman. Rounded grains are unusual but were noticed in the Catherine Hill Bay specimen. The garnet is usually colourless but may be very pale pink or very pale yellowish pink.

Magnetite occurs in many of the concentrates, but it is not confined to any special locality. In some places the octahedral crystals are preserved, but these may be rounded, or irregular grains alone may occur. In most concentrates alteration to limonite or hæmatite to varying degrees has taken place. Such grains with fresh cores are still attracted by the horseshoe magnet.

Pyrites. This mineral was present in nine of the specimens examined, and interesting differences of habit were noticed.

In the grit near the base of the Upper Marine at Bowenfels the pyrites was well crystallised in cubes of edge up to 0.5 mm. These crystals had large well developed cube faces with the pyritohedron commonly present. The

cube faces were sometimes striated. Clusters of such crystals occurred. Many of the crystal faces were dulled by oxidation but did not show bright tarnish colours.

Also in this concentrate tiny octahedral crystals of pyrites occurred. They were present, usually, as individuals and measured less than 0.1 mm. across.

In specimens from Wollongong groups of very tiny pyrites crystals occur encrusting other minerals such as quartz or iron oxide grains. The individual crystals measure much less than 0.1 mm. across. In one concentrate pyrites crystals or grains were enclosed by calcite, which was present as portion of the rock cement, showing that the authigenic pyrites had formed prior to the calcite.

The occurrence in the fine dark sandstone at Warden Head, Ulladulla, was particularly interesting. The concentrate contained numerous concretions; some a dull brownish colour, others yellow metallic, or dark, with red, purple, and blue tarnish. These concretions had a varying habit. Some were perfectly spherical while others showed bilateral symmetry. The latter varied from almost spherical grains with a shallow peripheral groove to those with a very deep groove almost separating the two practically spherical individuals (Plate II, Figs. 2 and 3). The outer layers of some had broken away, exhibiting a concentric structure in the outer layers surrounding a smooth core. In the case of the grooved concretions the central core was also grooved. The size of the spheres ranged from 0.03 mm. up to a maximum of 0.12 mm., averaging about 0.06 mm.

Several of the grains were crushed and treated microchemically with hydrochloric and nitric acids. The hydrochloric acid had no appreciable effect, disproving the presence of a carbonate in the dark concretions. With the nitric acid the metallic portions of the concretions went slowly into solution, leaving an earthy residue of hæmatite and limonite, the latter being more abundant. The solubility of the yellow metallic mineral in the nitric acid showed it to be pyrites (or marcasite, but definite distinction between the two, in this instance, was impossible). Some of the concretions consisted almost entirely of pyrites, while others were practically all iron oxide.

Spherical concretions from Warden Head, Ulladulla, have been recorded by Dr. Ida Brown.⁽⁷⁾ They occur embedded in the mudstone of the rock platform and measure about eight inches across.

Pyrites concretions were found also in a specimen from Shepherd's Hill, Newcastle, and from Bulli Point. Those with bilateral symmetry were fairly common in the former. Irregular grains were also present in the Newcastle specimen, and from Bulli irregular grains and aggregates of tiny crystals were recorded.

Grains of pyrites were present in one of the Coalcliff specimens, and aggregates of crystals were noted from East Maitland. (Plate II, Fig. 4.)

The crystallised character and concretionary form of the pyrites described show it to be probably of syngenetic origin.

Picotite. This mineral forms an important and interesting constituent in almost all the concentrates examined. Generally speaking it is more abundant in the South Coast Coal-measures, while it is common in the Northern Coal-measures and the few Branxton samples examined. It is rare in the majority of the Western Coal-measure and marine specimens, and in a few instances its presence is doubtful.

It occurs usually as lustrous black octahedral crystals and fractured grains. The octahedra may be modified by dodecahedra and more rarely by small cube faces. The crystal edges are sometimes worn and rounded but the crystals show remarkably little evidence of abrasion as a whole. Larger crystals (between 0.1 mm. and 0.2 mm. across) sometimes show tetrahedral elevations on the octahedral faces. Twinned crystals are frequently seen and such are more common in the northern area and the south coast (especially the coal-measures). In the Coalcliff samples several chains of crystals have been noticed. The average size (less than 0.1 mm.) of the picotite crystals from the western area is less than that from samples from other localities. The fractured grains are characterised by their conchoidal fracture, lustre, and reddish brown translucency on thin edge.

In the specimen from five feet above the Yard Seam, Shepherd's Hill, Newcastle, irregular fractured grains of a reddish brown mineral occur. These are wedge-shaped or rather platy, and are not quite similar to the typical fractured picotite grains. They gave the chromium reaction with a microcosmic salt bead. It is probable that these grains are chromite, but definite distinction from picotite is not possible. Typical cubic picotite crystals were also present in this concentrate.

Anatase. This mineral is widely distributed and occurs with varying habit. The most common habit is that of square tabular crystals flattened parallel to the (001) face. These occur as individual crystals of edge frequently less than 0.1 mm., or as aggregates of even smaller square bevelled plates. (Plate II, Figs. 5, 6, 8.)

The colour and diaphaneity of these square crystals vary. They may be almost colourless, white and opaque, light yellow or bright yellow, and clear or turbid to almost opaque. Light greenish yellow crystals were noticed from various localities and seem to be more frequent in concentrates from the west. They were present at Mt. Victoria, Ben Bullen, Mt. Bocoble, Wallerawang, Bowenfels and Gangerang Range. A similar greenish tint has been recorded in some of the South Coast Upper Marine specimens from Nowra and 11 miles north of Milton, but the Coalcliff Coal-measure specimens have dominantly a light yellow or cream-coloured variety.

Pale blue anatase, when present, generally is bipyramidal and diamond-shaped in habit, with horizontal striations. (Plate II, Fig. 7.) Blue crystals were more common in one of the Ben Bullen concentrates than in others. Yellow bipyramidal crystals also occur.

Granular anatase is frequently present in association with the crystallised mineral.

Some interesting composite grains showing anatase associated with other minerals have been recorded. Samples from Ben Bullen, Wallerawang, Mt. Bocoble, Yerranderie, Newcastle, Brunkerville, Mindaribba, and Termeil show aggregates of yellow platy crystals included in quartz grains, or bound together by secondary quartz (Plate II, Fig. 9.) Many of these grains have a dark core to the anatase aggregate, which is apparently the unaltered primary mineral from which the anatase is derived. The original mineral may be sphene, the breaking down of which would yield some silica, to form the matrix of the grain.

Other composite grains consist of minute anatase crystals coating granular anatase. The grains are frequently a dark reddish orange, or deep yellow colour, and sometimes have a black core (probably ilmenite). Examples of these grains have been noted from East Maitland, Coalcliff, and Myrtle Gully (six miles north of Milton).

Grains showing groups of anatase crystals embedded in leucoxene have been noted from Newcastle and Coalcliff.

The anatase is probably derived from ilmenite or sphene, and although there is no positive evidence in the concentrates examined, some of the anatase may be derived from the alteration of a titaniferous biotite.⁽⁵⁾

Rutile occurs in many of the concentrates. Most commonly it is present as oval grains, or slightly elongated rods. Clear crystals are fairly frequent. The colour is very variable in yellow, amber, orange, and red. Some of the crystals are perfectly clear, but many of the grains are quite cloudy, tending to become opaque. Several geniculate twins have been noted from Bowenfels, Wallerawang, Mt. Bocoble, Myrtle Gully, and Katoomba.

Examples of composite grains showing the alteration from rutile to ilmenite were noted from Branxton, East Maitland, Murrimba, and Ben Bullen. (Plate II, Figs. 10, 11.) In each case the alteration was more pronounced at the ends of the crystals or grains, the change commencing externally and working in along cleavage lines. This type of alteration is one of the commonest for rutile.⁽³⁹⁾

The change from rutile to ilmenite is reversible, and many of the cloudy, ill-shaped grains of rutile in these concentrates are thought to be secondary after ilmenite. Some may be secondary after sphene or other titaniferous minerals. "Transformations of the titanium minerals are possible in almost every direction."⁽¹⁵⁾

It was noticeable that the colour of the anatase, rutile and brookite in many of the concentrates was very similar.

Xenotime was definitely recognised in only two of the specimens examined—from near Mindaribba and Singleton.

It was found in the magnetic portion of the concentrate. In habit it is very similar to zircon, being present as slightly worn, elongated, tetragonal crystals. They are colourless to light yellowish in colour with some turbidity, which causes decrease in transparency. The crystals showed straight extinction but the interference figure was unobtainable.

Several grains were dissolved in a sodium carbonate bead and a very good phosphate reaction was obtained after treatment with nitric acid and ammonium molybdate.

Zircon. This mineral usually formed a high proportion of each concentrate. It was present as crystals or worn crystals. The degree of rounding varied in a single concentrate. Crystals from Tallong and Ulladulla showed excellent development of terminal faces, the faces (100), (110), (311), (111), (331), and (101) being recognised.

Some have very sharp terminations due to strong development of (311) faces.

Zoning was present in both the larger and smaller crystals. The zoning may be seen as contour zoning traced by fine lines (Plate II, Fig. 14) parallel to the surface, or inclusions may be arranged zonally. Zoned crystals have been observed from practically all localities. (Plate II, Fig. 15.)

Inclusions are very common in crystals and grains of all sizes. There may be tubular or rod inclusions frequently arranged parallel to the length of the crystal (Plate II, Fig. 16). Smaller zircons are often included in larger ones. Inclusions of a black opaque mineral are fairly common, and the cubic, octahedral habit of some of these has been noticed in specimens from Denman and Coalcliff; these are probably magnetite. In the coal-measure specimen from Mt. Bocoble yellow elliptical inclusions with a high refractive index have been noticed; these are possibly monazite.

The zircons are colourless, but very abundant fine dark inclusions and close zoning may give them a dirty brown or grey appearance, as in specimens from Ulladulla, Newcastle, Coalcliff, and others.

Zircons stained red by hæmatite⁽³²⁾ have been observed from Murrimba, Mt. Bocoble, and Bowenfels. The Mt. Bocoble zircons show a concentration of the red hæmatite around inclusions of decomposing iron oxide.

Purple zircons have been found in nearly all the Upper Marine concentrates examined from the South Coast, in several specimens from the coal-measures of the South Coast, and also from Bowenfels, Wallerawang, and Murrimba. The colour varies from a light mauve to a medium shade of purple, and a slight pleochroism has been noticed in these. The purple zircons are usually worn and rounded and rarely exhibit crystal form.

Apatite has a very interesting locality distribution. It occurs only in specimens from the north and in specimens from between Wollongong and Coalcliff. It is a common constituent in these South Coast sediments. It is entirely absent from all specimens from the west.

Apatite is present usually as slightly elongated or oval grains derived by the smoothing off of the crystal edges between the prisms and the terminal faces. *Apatites* from near Wollar and the South Coast quite frequently show

traces of the prism edges, and some terminal faces may be readily identified (Plate II, Fig. 18).

Grains terminated by the basal parting are common and thin hexagonal sections due to this parting have proved interesting.

Most of the apatites are colourless, but many of them are coloured by inclusions. The colour may be a light grey due to a few microscopic inclusions, or it may be a deep grey due to the crowding of these inclusions.

The arrangement of the inclusions varies. In many the vertical sections show a series of fine vertical lines, the inclusions being arranged in vertical planes parallel to the prism faces. Cross sections of these grains show intersecting lines of inclusions, often with a concentration of inclusions towards the margin of the grain (Plate II, Fig. 22).

These dust-like inclusions may be concentrated to a varying degree in a central core. Excellent examples of this were noted from Denman (Plate II, Figs. 19 and 20) and Scarborough. Inclusions are often concentrated along the parting lines.

In addition to the grey apatites, brown apatites are common. In some the coloration is apparently uniform but in others there is a concentration of colour along crystallographic planes or in concentric zones. Zonal structure is very well seen in cross section (Plate II, Fig. 21).

Both the grey and brown apatites are pleochroic, the strength of pleochroism depending on the depth of natural colour. The maximum absorption colour for some of the brownish apatites has a distinct red element in it.

Both varieties are attracted to different extents by the electro-magnet. This magnetic property and the appearance of some of the larger inclusions suggest that the inclusions are iron oxide. With very high power of the microscope the inclusions appear to be arranged in a bead-like fashion along crystallographic lines, and some appear to be surrounded by an earthy decomposition zone. The brown coloration is probably due to the change of these minute iron oxide inclusions to hematite or limonite, but in some cases there may be a chemical replacement of some of the calcium in the apatite by iron in the ferrous state.⁽³⁵⁾

Zirkel⁽⁴¹⁾ states that the yellow colour of some large apatites of Persian trachytes is due to long yellowish glass inclusions, and that these may be cryptoliths of cerium

phosphates. A microchemical test for cerium was carried out with brown apatites from near Wollar but without any positive result. A borax bead test for iron was attempted, also giving no positive result.

Ilmenite occurs rarely in the concentrates examined, but pseudomorphs of leucoxene and limonite after ilmenite were fairly common. Also it is very probable that much of the anatase and secondary rutile has been derived *in situ* from primary ilmenite as suggested by some of the composite grains.

When present the grains are black and irregular, and possess a metallic lustre.

Siderite was recognised only in the specimens examined from near the coal seams at Coalcliff and in the Upper Marine grit from near Bowenfels.

At Coalcliff it occurs as a cement and as tiny lenses in the rock. Some of it is black, due to included carbonaceous material. On treatment with hydrochloric acid it effervesced vigorously, leaving a black carbonaceous residue.

Siderite and carbonaceous siderite are not uncommon in coal-bearing shales and clays, and are formed by precipitation from stagnant water charged with iron salts and carbonates in solution.

Tourmaline is very widely distributed.

The colour is very variable in greens, browns and blues and combinations of these. Colour zoning is frequent in the South Coast Upper Marine specimens. Prismatic crystals are represented in almost every concentrate, although elliptical and rounded grains are the most common.

Black, opaque, dust-like inclusions are fairly common in the Upper Marine specimens from the South Coast. The inclusions may be grouped to form a core, or they may be zoned or arranged irregularly (Plate II, Figs. 23, 24).

The tourmaline crystals from the South Coast and Warrima are larger (from 0.2 mm. to 0.5 mm. in length) than many tourmalines from other localities. The tourmaline from the west average only about 0.1 mm. in length.

Barytes was recognised in only four concentrates from Brunkerville, Bulli Point, Wollongong, and Huskisson.

At Brunkerville no good crystals were observed, but irregular cleaved grains were present. These did not give good interference figures (Plate II, Fig. 31).

There was sufficient in the Brunkerville concentrate to confirm microscopic examination by a flame test for barium and a silver coin test for sulphur. Some of this barytes seems to be fibrous, and cloudy decomposition was fairly common. Decomposition in bands was common.

Idiomorphic cross sections were present in the Huskisson concentrate.

In the Wollongong concentrate it occurred as tabular crystals, flattened parallel to "c" (001), and with the domes (011) and (102) developed (Plate II, Fig. 30).

Brookite was present in six of the Upper Coal Measure specimens, and in fifteen of the Upper Marine specimens. Only a few crystals or grains were found in each concentrate. The habit was always that of plates flattened parallel to the (100) face. This face was usually striated vertically (Plate II, Fig. 28). The colour varied from almost colourless through various shades of yellow. Brookite was distinguished by its high R.I., its interference colours, and biaxial figure. It was always associated with anatase or rutile, and was undoubtedly formed authigenically by the alteration of a titanium mineral.

Monazite has an interesting locality distribution. It occurred only in the north-eastern specimens, in two specimens from Tallong, one from Bulli Point and in several from the South Coast Upper Marine Series.

It occurred characteristically as pale yellow rough-surfaced, worn grains. Many were elliptical with no trace of crystal faces. In monazite from Warrima, crystal faces may be detected. Here the grains measured up to 0.75 mm. by 0.3 mm., and the prismatic cleavage was well seen.

Inclusions (possibly zircon) were present in monazite grains from Branxton.

Slight decomposition was seen in most grains making them somewhat cloudy.

Hornblende was identified from only three localities, viz. Branxton, Tarro and Ben Bullen. It occurred as irregular grains showing two cleavages.

IX. THE SIGNIFICANCE OF SOME OF THE CONSTITUENT MINERALS.

Some remarks on the significance of a few of the heavy minerals seems necessary before discussing the source of the sediments.

Apatite. The apatite is confined to definite localities, and the presence of inclusions and colour in some of the grains is interesting.

Although I have found no written record of such inclusions or colour in apatite of New South Wales rocks, it is probable that they occur more commonly than one would expect from a microscopical examination of igneous rock slides. It is only by chance that these minor accessory minerals are revealed in microscope sections of any rock, and in order to determine the presence of these minerals the rock should be crushed, and the accessory minerals separated and concentrated by heavy liquids.

Colourless apatite may be present in practically any igneous rock, acid or basic. Records show that apatite with abundant inclusions, or coloured apatite, may also be present in different igneous rock types.

Some reference to the occurrence of apatite with numerous inclusions are: (a) Iddings^(24a)—"In some andesites and trachytes it occurs in comparatively large stout prisms, often coloured brown or bluish with abundant inclusions." (b) Lévy et Lacroix⁽²⁶⁾—"L'apatite des roches volcaniques renferme frequemment des granules violacés extrêmement fins." (c) Fleet and Smithson⁽²²⁾ and Simpson⁽³³⁾ describe dark apatite in granites and porphyries. (d) Skeats and Summers⁽³⁴⁾ record that in trachytes from Mt. Eliza "apatite with fibrous inclusions is abundant", and that at Sugarloaf Hill "apatite occurs sparingly with fibrous inclusions". (e) Mrs. H. M. Sherrard has shown me cross sections of apatite in slides of the Douro (No. 3) porphyry from Yass with inclusions arranged in intersecting lines.

Thus, apatite (colourless or with inclusions) could be derived from different varieties of igneous rocks.

An investigation of the accessory minerals of some of the Carboniferous flows to the north of the Kamilaroi sediments would be interesting in this connection.

Being comparatively soft, apatite would probably not survive more than one cycle of erosion, but come directly to the sediments from its parent igneous rock.

Picotite. This mineral occurs in practically all the concentrates examined. In some it is abundant, but in others it is represented by only a few crystals. The constant presence of picotite must be specially significant, since it is a rare constituent of sedimentary rocks, and has been recorded from very few localities elsewhere.⁽⁴⁾

An ultrabasic source for this mineral is essential, and the only known land rocks now exposed which could possibly supply the picotite are: (a) the Great Serpentine Belt trending in a N.W.-N.N.W. direction for a distance of about 250 miles and flanking the western and southern margin of the New England Plateau.⁽¹⁾ Related to this line of intrusions are smaller intrusions at Port Macquarie⁽¹³⁾ and on the Clarence River.⁽¹⁹⁾ (b) In the west there is a small serpentine intrusion at Lucknow.⁽³⁰⁾ (c) In the south-west serpentines outcrop along a line about 90 miles in length, trending in a N.N.W. direction, between Yarran-gobilly and Coolac.^(9a)

In connection with the occurrence of ultrabasic rock masses one may remark on the presence of ultrabasic xenoliths in many of the Tertiary dykes and intrusions of the South Coast and Sydney district. Ultrabasic xenoliths have been recorded from Pennant Hills Quarry,⁽²¹⁾ Hornsby and Dundas,^(2a) Moruya,^(8a) from a volcanic neck, Nepean River,⁽²⁸⁾ and from Kiama,⁽³⁷⁾

There seems to be no positive evidence that these are cognate xenoliths formed by the differentiation under plutonic conditions of the magma forming the host rock. Professor Browne makes the suggestion that they are early Tertiary differentiates included in the newer basic series.⁽¹⁰⁾

Card, describing several occurrences of ultrabasic rocks,⁽¹¹⁾ suggested that "masses of holocrystalline basic rock must exist at no great depth in this portion of Australia". Benson suggested a number of "small highly differentiated bodies" underlying the surface.^(2b) Dr. Ida Brown suggested the possibility of ultrabasic rocks below the surface "possibly in a complementary relationship to the enormous Devonian and Permian-Carboniferous batholiths of granite and granodiorite which outcrop over such a great area in eastern New South Wales".^(8b)

These xenoliths are all in rocks younger than the Kamilaroi rocks, and therefore could not help to supply the picotite, but they point to the possible existence of a large buried ultrabasic mass which could possibly outcrop in areas now covered by Kamilaroi and later sediments.

The known land masses of ultrabasic rock hardly seem adequate to explain the constant occurrence of the picotite crystals over such a large area and through such a great thickness of sediment.

For this reason one suggests the possibility of derivation of some of this material from outcrops now covered by sediments.

Part derivation from an easterly source—from Tasmantis⁽³⁸⁾—is also probable. "Tasmantis" is the name given to a land mass which existed to the east of the Australian continent in early Palæozoic times and which became united to the mainland towards the close of the Permo-Carboniferous period.

The proportion of picotite in specimens of the South Coast Coal-measures from Austinmer to Coalcliff is much higher than in specimens from other localities. Also, the crystals are well preserved, twins and chains of crystals are fairly frequent, and surface markings are preserved on the crystal faces. If the crystals had been carried for a great distance before deposition the twins and chains of crystals would probably have been broken into imperfect individuals, and the markings destroyed. In addition, the picotite in these concentrates is associated with apatite.

The nearest known large mass of ultrabasic rocks is that of the south-western zone referred to. This zone is about 160 miles from Coalcliff. Specimens from Tallong and the Upper Marine Series of the South Coast which are situated between this ultrabasic mass and Coalcliff have not a high proportion of picotite, but their source can be traced to closer rocks.

It seems impossible that the Coalcliff picotite and apatite are derived from the south-western rocks, but very probable that they came from Tasmantis.

Picotite, in the western sediments examined, is not common, but it is present rather as an accessory constituent. Probably it has been washed there by currents distributing the material from other parts of the sea or lake of deposition—from the north or east.

The Great Serpentine Belt to the north is of sufficient extent to supply the picotite present in the northern sediments.

X. THE SOURCE OF THE KAMILAROI SEDIMENTS.

In attempting to ascertain the source rocks of the sedimentary rocks one is confronted by the tremendous difficulty that practically no work has been done on the accessory minerals of the surrounding igneous rocks or the older sediments. All that can be done, therefore, is to

make a few suggestions to be confirmed or disproved later as the knowledge of accessory minerals is extended.

A study of Tables 1 and 2 and Plate I will show a natural division into four zones as determined by heavy mineral assemblages. These are: (1) the Northern and North-eastern Zone, including Wollar and Catherine Hill Bay; (2) the Western Zone, including Rylstone and Yerranderie; (3) the South-western and Southern Zone, including Tallong and Terneil; and (4) the South-eastern Zone, including Wollongong and Coalcliff.

(1) The Northern and North-eastern Zone.

The significant minerals determining this zone are garnet, apatite, monazite, and rare xenotime. These are present with picotite, zircon, tourmaline, titanium minerals and magnetite in most cases.

Garnet is not specially significant as directly indicating source rocks for the sediments. It is likely to be found in all kinds of rocks, igneous or metamorphic.^(24b) It is not known to what extent it is present in the Carboniferous rocks to the north of the Upper Marine Series and Upper Coal Measures, but it is present in the garnet gabbros in the Great Serpentine Belt.⁽³⁾ This is therefore a probable but not a proved source.

The origin of the apatite is uncertain.

Monazite and xenotime are derived from acid igneous rocks, especially granites. There are apparently no granites older than Kamilaroi in the district north of the sediments in question. The distribution of the monazite in the north-east suggests that they may have been derived from the north-east—perhaps from Tasmantis.

The picotite is derived partly, at least, from the Great Serpentine Belt.

Zircon, tourmaline, and rutile, as primary derivatives, are characteristic of acid and intermediate igneous rocks, and some metamorphic types. Being very resistant minerals, they are able to survive more than one cycle of erosion. They are probably present for redistribution in the Carboniferous sediments or flows. No distinctive features were noted which would enable one to use these minerals as definite index minerals.

From a consideration of the heavy mineral assemblages alone one would suggest a northerly and a north-easterly source for this area of deposition.

This is entirely in conformity with previous observations. According to David, "Marked diagonal bedding in the Newcastle Series, dipping to the south-west along the present meridional shore-line, proves the former existence of a land—Tasmantis—away out to sea to the east of Port Stephens"^(17b); also, "The land which supplied the Permo-Carboniferous sediments lay partly to the north, partly west, and partly to the east of the present coast line"^(18b).

(2) The Western Zone.

This zone is characterised by abundant zircon crystals, tourmaline, anatase and rutile, with rare picotite, and occasional magnetite, and some brookite. The assemblage (with the exception of the picotite) is typical of what one would expect from older sediments and to a lesser degree from acid rocks.

The presence of possible monazite inclusions in zircon from the Upper Coal Measures from Mt. Bocoble, and the presence of purple zircons in specimens from Bowenfels and Wallerawang, indicate a possible granitic source for some of the zircons. (Purple zircons do not occur in granites only, but a source from Devonian granites is being suggested for the South Coast Upper Marine Series, in which purple zircon is fairly frequent, and so it is thought that a similar source may have supplied the purple zircon at Mt. Bocoble.)

Titanium minerals (anatase, rutile, and brookite) are present, and are probably secondary after ilmenite or sphene. Sphene is a common constituent of the Hartley Devonian granite intrusion.⁽²⁵⁾

Monazite is absent from these concentrates, and the proportion of tourmaline slightly lower than in typical granitic types. Also the small grainsize of the western concentrates and the superabundance of zircon suggest that, for the most part, they have passed through more than one sedimentary cycle and are therefore probably derived from the old Devonian or Silurian sediments.

The picotite has probably been transported and distributed over the western area by currents in the sea or lake of deposition from localities where it was more abundant.

Carne, in discussing the derivation of the western Upper Marine strata, states, "The petrological character and structural arrangement of this great bed indicate

unmistakable deposition or proximity to the coastline of the Permo-Carboniferous sea". Referring to the derivation from the underlying Devonian system, he says: "Just as clearly also, do these sediments denote the source from which they have been derived. The boulders and pebbles are chiefly quartzite, and more rarely granite, porphyry and slate."⁽¹⁴⁾

The results of the heavy mineral investigation again gives additional evidence in support of previous observations.

(3) The South-western and Southern Zone.

The sediments of this zone have concentrates in part derived from an acidic igneous source.

They are characterised by the presence of abundant zircon, tourmaline with crystal shape usually well preserved and with occasional gaseous inclusions, clear reddish-brown rutile showing some crystal faces, and monazite is present in five of the South Coast Upper Marine specimens and in two specimens from Tallong. Secondary anatase is also present.

The main source rocks of these sediments are very probably the granitic rocks outcropping to the south-west and probably underlying a considerable area of the Upper Marine sediments. Source rocks of secondary importance would be the older sediments of Devonian, Silurian and Ordovician age.

Late Devonian granites outcrop at Marulan, Yalwal, Wandandian, Conjola, Moruya, and Braidwood.^(9b)

Sediments examined from Tallong, close to the Marulan granodiorite, had a slightly higher percentage of heavy minerals than other sediments. The concentrate from Warrima had no picotite, and monazite was more frequent than usual. This may be explained by the fact that the Glenrock granodiorite outcrops a few miles to the west.

Specimens from near Conjola (Nos. 26 and 27) have noticeably larger concentrates than others. This can be explained by the proximity of the Conjola granite.

The picotite may have been transported there by a minor drainage from the north-east (perhaps from the source suggested for group (4)), or its presence may be due to distribution by currents and drift in the area of deposition.

Harper, in dealing with the direction of drainage of the South Coast Upper Marine Series, says: "Probably a

precipitous mountain range existed in the south and south-west of the Upper Marine sea, with its axis trending from eastwards of Bateman's Bay, north-westerly to beyond Goulburn. The precipitous nature of the range is indicated by the large angular blocks of slate found in the basal beds of the Marine Series along their southern edge. This range provided one of the watersheds from which the sediments were derived, and the confines of the sea would be extended further and further to the south and west as denudation and continued subsidence proceeded. As a consequence an overlap occurs, and the basal beds at the periphery of the Marine Series are not so old as those occupying a more central position."^(23d)

Devonian granites, of which the Yalwal, Wandandian, and Conjola exposures remain, on the north-easterly side of this ancient mountain range, probably furnished, in part, the first heavy mineral assemblages in the Upper Marine sediments. More of the resistant minerals such as zircon, tourmaline, and rutile would be added later when the dominant drainage was from the older sedimentary quartzites and slates, representatives of which are found as boulders in some of the basal beds in the south-west. Further erosion of the mountain range to the south-west would probably bring the Braidwood and Araluen granites into the drainage area.

(4) The South-eastern Zone.

The concentrates from the Wollongong-Coalcliff area differ from the others in containing abundant picotite associated with apatite, which is common. As already pointed out the picotite was represented by perfect crystals, twinned crystals, and groups of crystals, which had not been disintegrated by transport. The apatite occurred as slightly worn elongated grains in some of which the prisms and terminal faces could be recognised. Other minerals present were zircon, tourmaline, and titanium minerals.

The abundance and preservation of both the picotite and apatite suggest a source from somewhere to the east, from the southerly extension of Tasmanis.

Harper suggests for the Southern Coal Measures a south-west to north-easterly drainage, as indicated by the "wash-outs" in the coal-measures at Mount Kembla.^(23d) This direction is practically the reverse of what is suggested

by the heavy mineral concentrates of the Wollongong-Coalcliff area.

More detailed work on the heavy minerals of the coal-measures from the coastal range is necessary to confirm or disprove a source from east of the present coastline, but from the number of specimens now examined it seems impossible to explain the proportion of picotite and apatite except by assuming drainage from the east.

The most probable explanation is that the streams drained in from a south-westerly or southerly direction in the south-west and south, draining the same rocks as for the Upper Marine Series, and that the south-easterly and easterly coal-measures were fed from a south-easterly or easterly source.

XI. A BRIEF COMPARISON OF THE HEAVY MINERALS OF THE KAMILAROI SEDIMENTS AND THE TRIASSIC NARRABEEN SEDIMENTS.

Consulting the tables of mineral distribution (pp. 360-1) of the paper on the Mineralogy of the Narrabeen Series,⁽¹⁶⁾ and comparing them with Tables 1 and 2 of this paper, one can detect certain similarities in mineral assemblages.

The Narrabeen sediments may be considered as belonging to three groups: (1) those from north of Broken Bay, (2) those from the west (Blue Mountain area), and (3) those from the South Coast.

The concentrates from sediments between Terrigal and Tuggerah are similar to those of zone (1) of the Kamilaroi, bearing garnet, apatite (colourless and coloured), and monazite. Thus the northern zone of the Kamilaroi could be extended to include these Narrabeen sediments.

Similarly, the specimens from Katoomba, Blackheath, and Mt. Victoria have the same mineral assemblages as the western Kamilaroi.

In specimens from between Bulli and Garie picotite is common, but they differ from the Southern Coal-measure group in the absence of apatite from the former except from one specimen from Bulli. The preservation of apatite, however, is dependent on conditions of sedimentation, and the texture (compactness and porosity) of the consolidated rock. The absence of apatite in certain specimens does not necessarily mean that the mineral had not ever been present. In fact, the presence of apatite in the one specimen from Bulli rather suggests

that apatite may have been present in others, having been dissolved since the time of deposition.

The other constituent minerals of the Narrabeen and Kamilaroi sediments from this area are comparable.

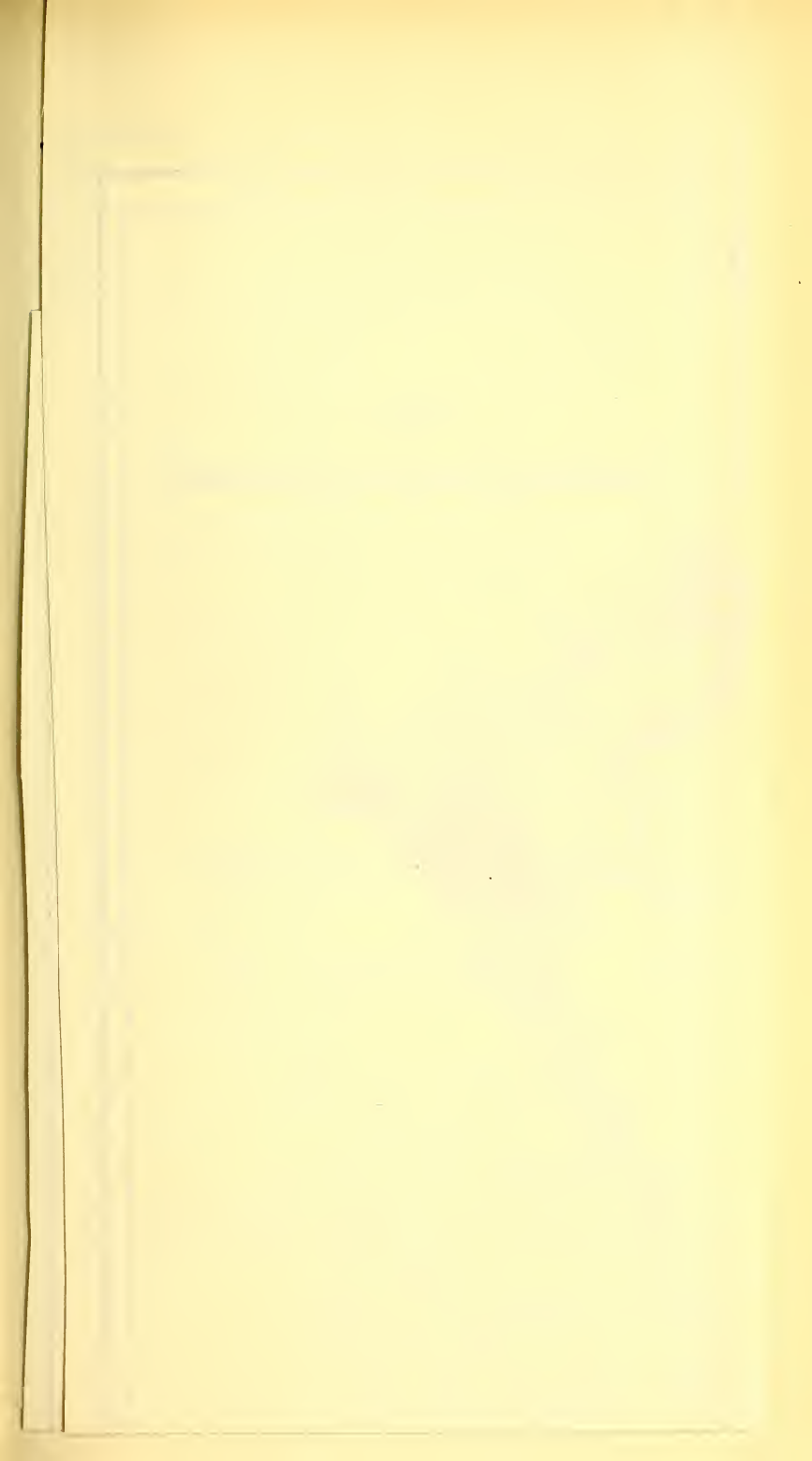
Thus this area of Narrabeen sediments can be classed with zone (4) of the Kamilaroi rocks.

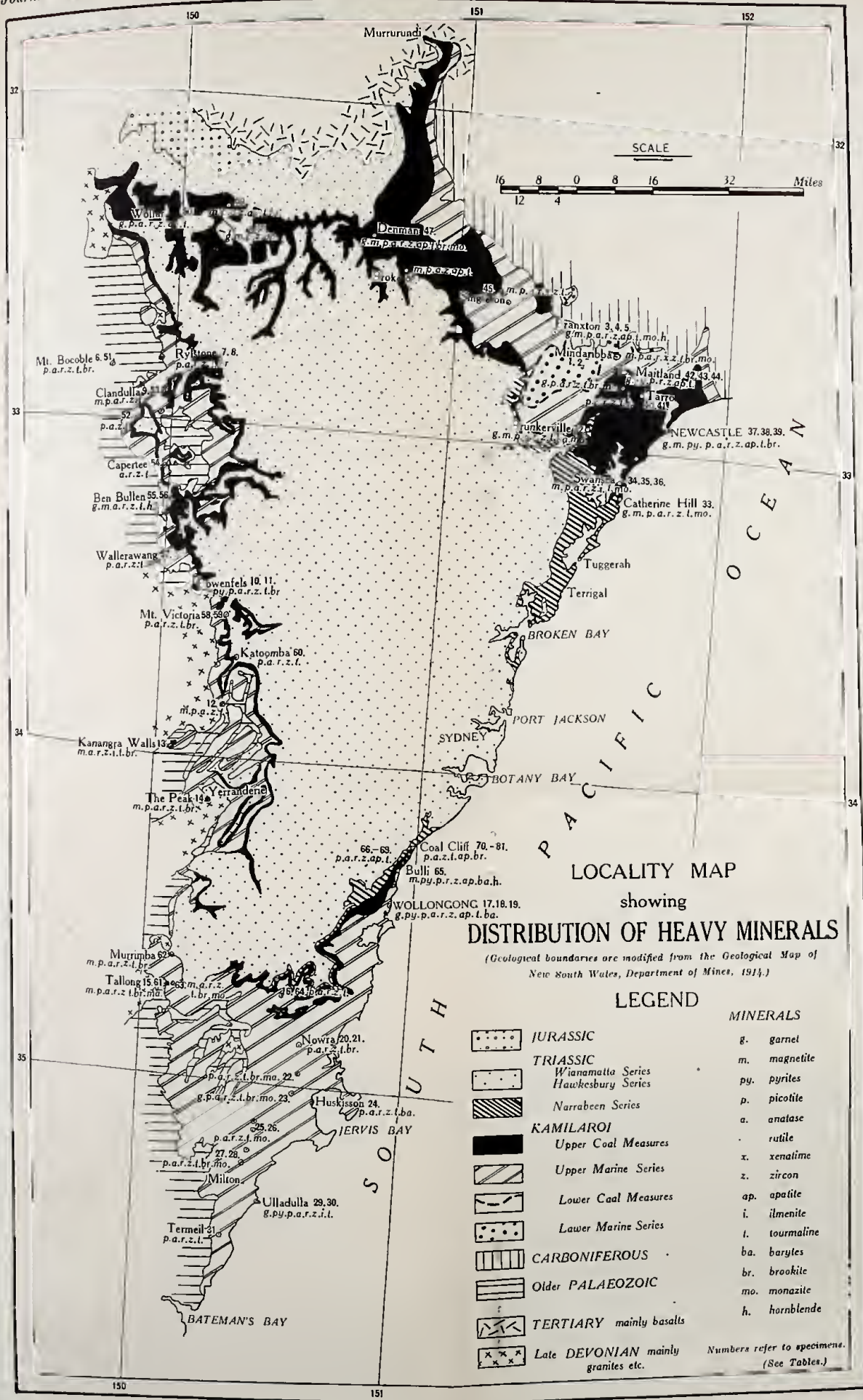
The Narrabeen sediments of these three groups have apparently been derived from the same source rocks as the Kamilaroi. Those from the north of Broken Bay have possibly come from a north-easterly direction, from Tasmanis, the western Narrabeen sediments from the older sediments, and in part, the Devonian granite from the west of the mountain range, and the South Coast specimens from an easterly or south-easterly source. They also probably represent to a certain extent redistributed Kamilaroi sediments.

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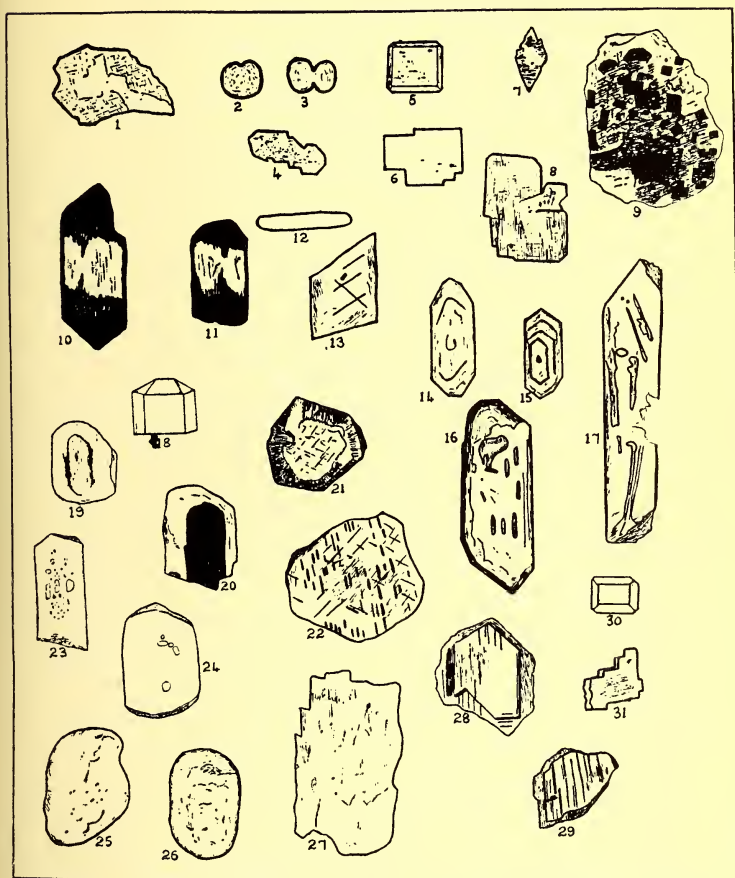
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EXPLANATION OF FIGURES 1-31, PLATE II.

1. Garnet, irregular grain, Branxton. $\times 100$.
2. Pyrites concretion, Warden Head, Ulladulla. $\times 100$.
3. Pyrites concretion showing bilateral symmetry, Warden Head, Ulladulla. $\times 100$.
4. Pyrites, group of crystals, East Maitland. $\times 100$.
5. Anatase crystal, tabular habit, Murrimba. $\times 45$.
6. Anatase showing "stepped" edges, Ben Bullen. $\times 100$.
7. Anatase, bipyramidal crystal, Katoomba. $\times 100$.
8. Anatase, Mt. Victoria. $\times 100$.
9. Anatase crystals in quartz grain, showing remains of decomposing mineral, Ben Bullen. $\times 100$.
10. Rutile altering to ilmenite, Branxton. $\times 100$.
11. Rutile altering to ilmenite, cleaved plate, Ben Bullen. $\times 100$.
12. Rutile, typical rod shape, Tallong. $\times 100$.
13. Rutile, cleaved plate, showing cleavage lines, Nowra. $\times 100$.
14. Zircon, zoned, Parma Creek. $\times 100$.
15. Zircon, zoned by fine inclusions, Bowenfels. $\times 100$.
16. Zircon, showing inclusions, Tallong. $\times 100$.
17. Zircon, showing irregular tubular inclusions, Mt. Victoria. $\times 100$.
18. Apatite, showing crystal faces and basal parting, 19 miles east of Wollar. $\times 45$.
19. Apatite, slightly worn crystal showing central core of dust-like inclusions, Denman. $\times 100$.
20. Apatite, slightly worn crystal showing very dense central core of dust-like inclusions, Denman. $\times 100$.
21. Apatite, basal section of brown apatite, showing zoned inclusions and inclusions parallel to crystal faces, Newcastle. $\times 100$.
22. Apatite, cross section of grey apatite showing inclusions arranged in crystallographic planes—inclusions are denser along one set of planes, 19 miles east of Wollar. $\times 100$.
23. Tourmaline with iron oxide and gas inclusions, Termeil. $\times 100$.
24. Tourmaline with gas inclusions, Murrimba. $\times 100$.
25. Monazite, worn grain, Parma Creek. $\times 100$.
26. Monazite, worn grain, Brunkerville. $\times 100$.
27. Hornblende, Ben Bullen. $\times 100$.
28. Brookite plate showing crystal edges and vertical striations, Murrimba. $\times 100$.
29. Brookite plate, almost colourless, showing vertical striations, Mt. Victoria. $\times 100$.
30. Barytes, tabular crystal, Wollongong. $\times 100$.
31. Barytes, cleaved fragment, Brunkerville. $\times 100$.

ISONITROSO α -THUJENE.

By ARTHUR JOHN BIRCH, M.Sc.

(Manuscript received, July 20, 1938. Read, August 3, 1938.)

It is well known that α -pinene nitrosochloride (I) readily loses hydrochloric acid to give isonitrosopinene (II) (cf. Wallach, *Ann.* 268, 198; Ruzicka and Trebler, *Helv. C.A.*, 4, 568), and it seemed of interest to examine α -thujene nitrosochloride (III) in order to see if it would yield the corresponding isonitroso α -thujene (IV). This substance is an isomer of carvacrylhydroxylamine (V) and should be readily convertible to this substance or its alteration products.

It has, in fact, been found possible to remove hydrochloric acid from α -thujene nitrosochloride by the action of pyridine and obtain a substance which is probably (IV). This by the action of cold concentrated hydrochloric acid for a short time yields a substance probably represented by the formula (VI) while hot concentrated hydrochloric acid alters both (IV) and (VI) to 2-methyl-4-chloro-5-isopropyl aniline (VII). By the action of 50% sulphuric acid on either (IV) or (VI), *p*-aminothymol (VIII) is produced. This can be prepared in an exactly similar manner from carvoxime, but it has not been found possible to prepare the amine (VII) by the action of concentrated hydrochloric acid on the latter, since hydrolysis takes place with ultimate formation of carvacrol.

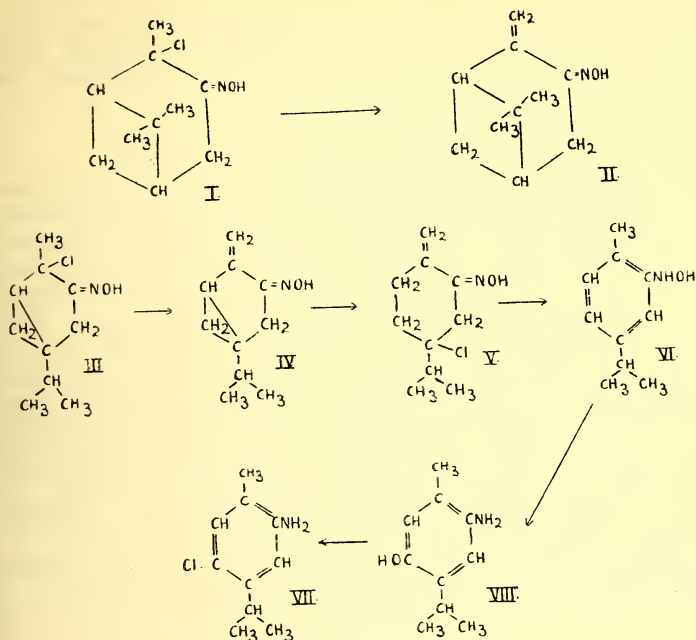
The mechanism of these changes is outlined below.

The conversion of phenylhydroxylamine to *p*-aminophenol by the action of sulphuric acid, and to *p*-chloroaniline by the action of hydrochloric acid has been observed by Bamberger (*Ber.*, 27, 1349, 1552; 28, 251).

EXPERIMENTAL.

di- α -thujene nitrosochloride.

This was prepared by the method given by Birch (*J. Proc. Roy. Soc. N.S.W.*, 1937, 71, 333), the yield from 60 ml. of purified α -thujene fraction being 23 g.

Isonitroso α -thujene.

α -thujene nitrosochloride (23 g.) and pyridine (30 ml.) were mixed, water (50 ml.) added, and the pasty mass heated on the water bath for fifteen minutes. The clear yellow liquid was then poured into water (200 ml.) and extracted three times with ether (100 ml.). The product so obtained (14 g.) was allowed to stand in a vacuum desiccator for three days in order to remove traces of pyridine. It was a pale yellow viscous oil, which could not be crystallised. Found: N, 8.4%; calc. for $C_{10}H_{15}NO$, N, 8.5%. On attempting to distil at 2 mm. the substance decomposed, yielding deep red products boiling over the range 115°-150°.

Compound VI.

Isonitroso α -thujene (10 g.) was rapidly dissolved in concentrated hydrochloric acid (50 ml.), the solution allowed to stand for five minutes, poured into water, and excess sodium acetate added. The oil which separated was extracted by means of ether, and allowed to stand. It partially crystallised, and was drained on a porous tile and

recrystallised from a mixture of petroleum ether and ethyl acetate. Yield, 2 g.; beautiful colourless plates, m.p. 149°. Found: N, 7.4%; Cl, 17.2%; calculated for $C_{10}H_{16}NOCl$, N, 7.0%; Cl, 17.6%.

2-Methyl-4-chloro-5-isopropyl aniline.

(A) Compound VI (5 g.) and concentrated hydrochloric acid (20 ml.) were refluxed for an hour, the solution steam distilled to remove a small amount of volatile material, and cooled in ice. A mass of colourless needles separated, mixed with a little tar, and was filtered off and recrystallised from aqueous alcoholic hydrochloric acid. M.p., 207°. The free amine was prepared from this hydrochloride by treatment with excess 20% caustic soda, followed by ether extraction and distillation. Colourless liquid, b.p. 115°-120°/25 mm. Yield, 2.5 g. Acetyl derivative, m.p. 105°; found: N, 6.3%; calculated for $C_{12}H_{16}NOCl$, N, 6.2%. Benzoyl derivative, m.p. 128°; found: N, 5.0%; calculated for $C_{17}H_{18}NOCl$, N, 4.9%. Picrate, yellow needles, m.p. 165°.

(B) Isonitroso α -thujene (10 g.) by an exactly similar process yielded *p*-chlorocarvacrylamine (5 g.).

p-Aminothymol.

(A) Compound VI (5 g.) and 50% sulphuric acid (15 ml.) were heated on the water bath for thirty minutes, cooled, a little oily material extracted by ether, and the acid neutralised with sodium hydroxide. The precipitated compound was taken up in ether, the ether evaporated, and the residue recrystallised from toluene. Colourless plates, m.p. 175°, darkening in air. Mixed melting point with an authentic sample prepared from carvoxime by the method of Wallach (*Ann.*, 346, 271), 175°.

(B) Isonitroso α -thujene (10 g.) by an exactly similar process also gave *p*-aminothymol (2.5 g.).

ACKNOWLEDGMENTS.

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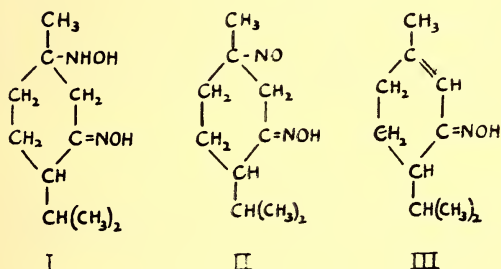
The University of Sydney.

1-NITROSOMENTHONE OXIME AND ITS DECOMPOSITION.

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and J. G. MCKEAN.

(Manuscript received, July 20, 1938. Read, August 3, 1938.)

The hydroxylamino-oxime of piperitone (I) yields a nitroso-compound on oxidation (Baker and Smith, "Research on the Eucalypts", 2nd Edition, p. 392). This nitroso-compound (II) has now been isolated and studied. When first prepared it melts at 124°-125° C., but the melting point soon falls on keeping. After ten months under ordinary laboratory conditions a preparation was found to have lost the properties of a nitroso-compound and to consist mainly of piperitone oxime (III) together with some resinous material.



The reaction which had taken place seemed therefore to amount to the splitting off of hyponitrous acid, HNO, from the nitroso-oxime. Hyponitrous acid is unstable and breaks down easily to nitrous oxide and water, so that nitrous oxide might be expected as one of the products when the nitroso-oxime decomposes (cf. Anderson and Hammick, *J. Chem. Soc.*, 1935, 1679). The decomposition was found to be accelerated by the influence of heat. Working under carefully controlled conditions nitrous

oxide was collected and identified. The amount obtained was 34.2 per cent. of that which would be produced by a quantitative decomposition into oxime, nitrous oxide and water. The solid residue remaining after the decomposition consisted principally of piperitone oxime which was recovered readily on recrystallisation.

EXPERIMENTAL.

Piperitone hydroxylamino-oxime.

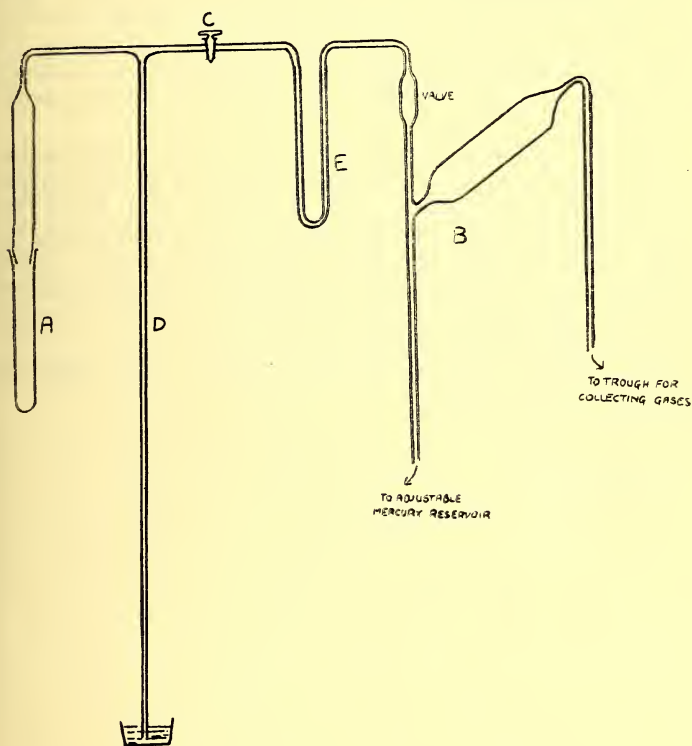
This was prepared by a modification of the method described by Read and Smith (*J. Chem. Soc.*, 1921, 119, 783). Redistilled piperitone (6 g.) was dissolved in methylated spirit (18 ml.) and a solution containing caustic potash (6 g.) in water (3 ml.) added. The mixture, which became brown, was heated to 75° C. on a water bath and a solution of hydroxylamine hydrochloride (6 g.) in water (6 ml.) added slowly. After heating to boiling under a reflux condenser for 15 minutes the whole reaction mixture was evaporated to dryness on the water bath. The residue was treated with water to remove potassium chloride and was then washed several times with several small quantities of alcohol. The product so obtained melted at 171° C. and was sufficiently pure for the preparation of the nitroso-compound. The yield was about 40 per cent., calculated on the piperitone used, but it was not found possible to obtain this yield when working with larger quantities than those given. A specimen of the product, recrystallised from alcohol and ether, melted at 174° C.

1-nitroso-menthone oxime.

Piperitone hydroxylamino-oxime (6 g.) and yellow mercuric oxide (12 g.) were intimately mixed and chloroform (70 ml.) added. The mixture was boiled under a reflux condenser for two hours, after which it was cooled and immediately filtered. On being allowed to stand, the filtrate deposited a pale blue crystalline material (3 to 3.5 g.). It melted, when freshly prepared, at 124°-125° C. to a blue liquid. Found: nitrogen, 13.7 per cent.; calculated for $C_{10}H_{18}N_2O_2$, 14.1 per cent. The substance was sparingly soluble in alcohol or ether, more so in benzene, toluene, or chloroform, the solutions being blue or green in colour. When it was heated with either alcoholic potash or alcoholic sulphuric acid, piperitone oxime was obtained.

Thermal Decomposition of the Nitroso-oxime.

The decomposition of the nitroso-oxime was studied under conditions which allowed the gaseous products to be collected and examined. The apparatus used was as illustrated.



A weighed quantity of the nitroso-oxime was introduced into the tube A, and the whole apparatus exhausted by means of the mercury pump B. The stopcock C was then closed and the tube containing the nitroso-oxime heated at 116° C. with an oil bath for 45 minutes, by which time the mercury in the manometer D had ceased to fall. The U-tube E was then immersed in liquid air and the stopcock opened sufficiently to allow a slow stream of gas to pass through. When the manometer ceased to indicate any change in pressure, the apparatus was exhausted again by the pump and the uncondensed gas collected in a graduated

tube over mercury. It was identified as nitrogen. The liquid air bath was then removed, the condensable gases being pumped off and collected. As far as could be determined, this material consisted of nitrous oxide. It was colourless, did not go brown on mixing with air, and supported the combustion of phosphorus with a very slight diminution of volume. It was slightly soluble in water but not in caustic potash solution. In estimating the weight of nitrous oxide produced, allowance was made for the water produced as a simultaneous decomposition product.

In a typical experiment 0.2412 gm. of nitroso-oxime gave 0.5 ml. of non-condensable gas and 14 ml. of condensable gas, both measured at 25° C. and 300 mm. The solid residue weighed 0.2208 gm. From these data, the weight of dry N_2O obtained was 0.009152 gm., corresponding to 34.2 per cent. of that which would be produced by a quantitative decomposition. From the residue, piperitone oxime was readily recovered.

The authors' thanks are due to Dr. J. E. Mills for assistance and advice.

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COORDINATION COMPOUNDS WITH 8-AMINO-
QUINOLINE AS A CHELATE GROUP.By GEORGE J. BURROWS, B.Sc.,
and ERNEST RITCHIE, B.Sc.

(Manuscript received, August 17, 1938. Read, September 7, 1938.)

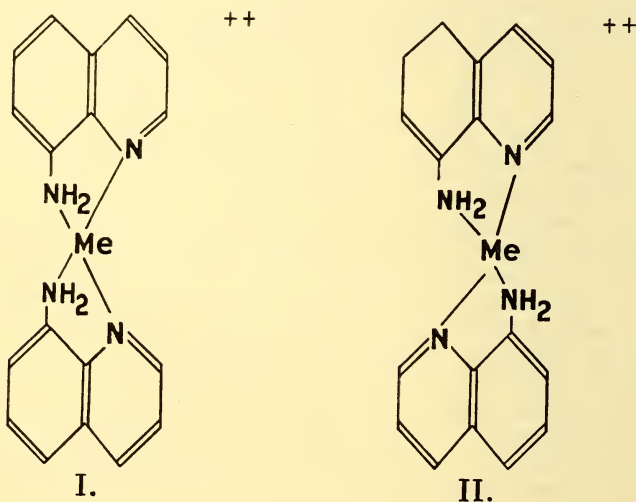
The coordination compounds of several unsymmetrically substituted ethylene diamines with certain tetravalent metals have been prepared and studied in recent years. Reihlen and his co-workers (*Annalen*, 489, 42; 499, 144) claimed to have resolved the bis (1·2 isobutylene diamine) platinous and palladous ions and the bis (2-aminomethyl-3-methyl-4-ethyl quinoline) platinous, palladous and nickel ions by fractional crystallisation of the bromocamphor-sulphonates. They have also used phenyl ethylene diamine in similar resolution experiments (*Annalen*, 519, 80; 520, 256). Further, claims to have effected resolution of palladous and platinous ions by the use of 2·3 diaminotoluene have been made by Rosenheim and Gerb (*Z. anorg. allgem. Chem.*, 210, 289). It is remarkable, however, that in no case have nickel, platinous, or palladous salts been obtained in optically active forms after removal of the bromocamphor sulphonic acid used in the resolution. The results, however, do indicate that the valences in tetravalent platinum, nickel, and palladium may be tetrahedrally disposed under certain circumstances.

On the other hand, the planar distribution of the valences in tetravalent metals finds many supporters. Cox (*J.C.S.*, 1932, 1912) concluded from X-ray measurements that the four nitrogen atoms and the platinum atom in tetrammine platinic chloride monohydrate are coplanar, whilst Hantzsch (*Ber.*, 59, 2761) upholds Werner's original hypothesis (*Z. anorg. allgem. Chem.*, 3, 316) that the two isomeric forms of dichlorodiammine platinum are cis and trans isomers.

Mills and Quibell (*J.C.S.*, 1935, 839) also concluded that the valences of tetravalent platinum are coplanar, and produced very strong evidence in favour of their contention by their resolution of mesostilbenediamineisobutylene-

diamine platinum chloride, which would have a plane of symmetry if the four covalences of platinum were tetrahedrally disposed, but not if they were coplanar. Several other important contributions supporting both sides of this question have been made (see Bailar, *Chemical Reviews*, 1936, 19, 67).

As a further contribution to this subject the authors describe a preliminary investigation of the coordination compounds in which 8-aminoquinoline acts as the chelate group. If the four valences of a tetravalent metal are planar, cis (I) and trans (II) forms should exist, but if the valences are tetrahedrally disposed, optically active forms should be obtainable. At the outset it may be stated that no sign of cis-trans isomerism was detected. In each case the complex compound was apparently homogeneous. The results of attempts to resolve certain of these will be reported later.



Copper salts coordinate readily with 8-aminoquinoline with evolution of heat, bis or mono-derivatives being obtained according to the amount of amine used. The bis salts are blue and the mono green. The green mono (8-aminoquinoline) copper nitrate, however, has only a momentary existence, decomposing even in the presence of excess copper nitrate to the blue bis (8-aminoquinoline) copper nitrate and copper nitrate.

Two series of nickel salts are also obtainable. Those of the bis series have a violet colour, whilst those of the mono series are bluish-grey. They are rather more soluble in water than the corresponding copper salts and do not form as rapidly, but are quite as stable. Cobalt chloride, the only cobalt salt examined, forms only a brown bis derivative even when only a small amount of 8-aminoquinoline is treated with excess cobalt chloride.

Ferrous salts form both types of compounds, but, surprisingly enough, the brown bis compound is very unstable and decomposes before it can be dried. The yellow mono salt is quite stable. Ferric salts oxidise the amine to a black tar. Manganous and chromic salts do not coordinate with 8-aminoquinoline.

The coordination compounds form crystalline powders which are slightly soluble in water but insoluble in alcohol and other organic solvents. Their aqueous solutions are decomposed by warming, precipitating the metallic hydroxide, and even by standing at room temperature for some time. Dilute acids and alkalis decompose them easily.

EXPERIMENTAL.

8-Aminoquinoline.

The 8-aminoquinoline was prepared in 60% yield by the reduction of 8-nitroquinoline with iron powder and 50% acetic acid at 50° C. (Dikshoorn, *Rec. Trav. Chim.*, 1929, 48, 147).

M.pt., 65° C.; b.pt., 174° C./26 mms.

The complex compounds were made by mixing concentrated solutions of the metallic salt in water and the amine in alcohol, at room temperature. After standing half an hour the precipitate was filtered off and dried in the air.

(a) Copper salts.

(i) Copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) (5 g.) 1 mol. and 8-aminoquinoline (5.8 g.) 2 mols. gave a bright blue crystalline precipitate immediately.

Found: Cu, 11.0%; SO_4 , 16.9%.

Calculated for $(\text{Cu}(\text{C}_9\text{H}_8\text{N}_2)_2)\text{SO}_4 \cdot 7\text{H}_2\text{O}$: Cu, 11.1%; SO_4 , 16.7%.

(ii) Copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) (5 g.) 1 mol. and 8-aminoquinoline (2.9 g.) 1 mol. gave a green precipitate at once.

Found: Cu, 16.4%; SO_4 , 24.1%.

Calculated for $(\text{Cu}(\text{C}_9\text{H}_8\text{N}_2))\text{SO}_4 \cdot 5\text{H}_2\text{O}$; Cu, 16.3%; SO_4 , 24.4%.

(iii) Cupric chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) (3.4 g.) 1 mol. and 8-aminoquinoline (5.8 g.) gave a pale blue precipitate at once.

Found: Cu, 12.5%; Cl, 13.8%.

Calculated for $(\text{Cu}(\text{C}_9\text{H}_8\text{N}_2)_2)\text{Cl}_2 \cdot 5\text{H}_2\text{O}$: Cu, 12.4%; Cl, 13.8%.

(iv) Cupric chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) (3.4 g.) 1 mol. and 8-aminoquinoline (2.9 g.) 1 mol. gave a bright green crystalline precipitate.

Found: Cu, 21.9%; Cl, 24.0%.

Calculated for $(\text{Cu}(\text{C}_9\text{H}_8\text{N}_2))\text{Cl}_2 \cdot \text{H}_2\text{O}$: Cu, 21.7%; Cl, 23.9%.

(v) Copper nitrate ($\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (4.8 g.) 1 mol. and 8-aminoquinoline (5.8 g.) 1 mol. gave a blue precipitate.

Found: Cu, 10.9%.

Calculated for $(\text{Cu}(\text{C}_9\text{H}_8\text{N}_2)_2)(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$: Cu, 10.95%.

(b) Ferrous salts.

(i) Ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) (5.56 g.) 1 mol. and 8-aminoquinoline (5.76 g.) 2 mols. gave after about 15 minutes a brown precipitate which rapidly decomposed, becoming almost black.

(ii) Ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) (5.56 g.) 1 mol. and 8-aminoquinoline (2.88 g.) 1 mol. quickly gave a bright yellow precipitate.

Found: Fe, 13.9%; SO_4 , 23.6%.

Calculated for $(\text{Fe}(\text{C}_9\text{H}_8\text{N}_2))\text{SO}_4 \cdot 6\text{H}_2\text{O}$: Fe, 13.9%; SO_4 , 23.8%.

(c) Nickel salts.

(i) Nickel chloride ($\text{NiCl}_2 \cdot 2\text{H}_2\text{O}$) (3.32 g.) 1 mol. and 8-aminoquinoline (5.76 g.) 2 mols. after 20 minutes on scratching with a glass rod gave a violet crystalline precipitate.

Found: Ni, 12.8%; Cl, 15.5%.

Calculated for $(\text{Ni}(\text{C}_9\text{H}_8\text{N}_2)_2)\text{Cl}_2 \cdot 2\text{H}_2\text{O}$: Ni, 12.9%; Cl, 15.6%.

(ii) Nickel chloride ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$) (4.75 g.) 1 mol. and 8-aminoquinoline (2.88 g.) 1 mol. gave a pale bluish-grey precipitate.

Found: Ni, 10.5%; Cl, 12.8%.

Calculated for $(\text{Ni}(\text{C}_9\text{H}_8\text{N}_2))\text{Cl}_2 \cdot 16\text{H}_2\text{O}$: Ni, 10.5%; Cl, 12.6%.

(iii) Nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (4.57 g.) 1 mol. and 8-aminoquinoline (5.76 g.) 2 mols. gave a pale violet precipitate.

Found : Ni, 10.7%.

Calculated for $(\text{Ni}(\text{C}_9\text{H}_8\text{N}_2)_2)(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$: Ni, 10.8%.

(iv) Nickel nitrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) (4.57 g.) 1 mol. and 8-aminoquinoline (2.88 g.) 1 mol. gave a pale bluish-grey precipitate.

Found : Ni, 11.4%.

Calculated for $(\text{Ni}(\text{C}_9\text{H}_8\text{N}_2))(\text{NO}_3)_2 \cdot 10\text{H}_2\text{O}$: Ni, 11.6%.

(d) Cobalt salts.

Cobalt chloride ($\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) (4.76 g.) 1 mol. and 8-aminoquinoline (5.76 g.) 2 mols. gave a pale brown precipitate after about 20 minutes.

Found : Co, 13.1% ; Cl, 15.5%.

Calculated for $(\text{Co}(\text{C}_9\text{H}_8\text{N}_2)_2)\text{Cl}_2 \cdot \text{H}_2\text{O}$: Co, 13.0% ; Cl, 15.6%.

ACKNOWLEDGMENT.

One of the authors (E.R.) desires to express his grateful acknowledgment to the University of Sydney for a Science Research Scholarship which enabled him to take part in the above investigation.

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NOTE ON THE PREPARATION OF p-TOLYL
STIBINIC ACID.By GEORGE J. BURROWS, B.Sc.,
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(Manuscript received, August 17, 1938. Read, September 7, 1938.)

The method of Goddard and Yarsley (*J.C.S.*, 1928, 721) for the preparation of p-tolyl stibinic acid affords but poor yields (less than 15%), and is, moreover, rather tedious. An improved method has now been devised which consistently gives yields of 45-50%. The details are as follows :

The diazo solution from p-toluidine (39 g.), concentrated sulphuric acid (30 c.c.), sodium nitrite (27 g.), and water (350 c.c.) was added slowly and with vigorous stirring at 0° to the sodium antimonite solution prepared by mixing a solution of antimony trichloride (85 g.) in concentrated hydrochloric acid (20 c.c.) and glycerol (20 c.c.), with sodium hydroxide (120 g.) in water (4,000 c.c.). During the addition of the diazo solution the temperature was not allowed to exceed 0°. Excessive frothing was prevented by the addition of small amounts of ether from time to time.

After standing overnight at room temperature, the reaction mixture was filtered from coloured by-products, nearly neutralised with dilute hydrochloric acid, and then treated with carbon dioxide until antimony trioxide was no longer precipitated. This was filtered off and the p-tolyl stibinic acid precipitated from the filtrate with hydrochloric acid. After drying and recrystallising from alcohol the yield was 50 grammes. (Theoretical=99 grammes).

Found : Sb=46.2%.

Calculated for $C_7H_9O_3Sb$, Sb=46.3%.

ACKNOWLEDGMENT.

One of the authors (E.R.) desires to express his grateful acknowledgment to the University of Sydney for a Science Research Scholarship, which enabled him to take part in the above investigation.

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DERIVATIVES OF TETRONIC ACID.

By FRITZ REUTER, D.Phil., A.A.C.I.,*
and RICHARD B. WELCH, B.Sc.

(Manuscript received, August 23, 1938. Read, September 7, 1938.)

When *Penicillium Charlesii* G. Smith is grown on a medium containing glucose and inorganic salts, there are formed d- γ -methyl-tetronic acid (I) (Clutterbuck *et al.*⁽⁷⁾), carolic acid (II), and carolinic acid (III), together with other metabolic products (Clutterbuck *et al.*⁽⁴⁾). The compounds II and III are closely related to I, II (in its hydrated form) and III, being α -(γ -hydroxy-butyryl)- and α -(β -carboxy-propionyl)- γ -methyl-tetronic acids respectively (Clutterbuck *et al.*⁽⁵⁾). If II and III are treated with hydrogen in the presence of palladinised charcoal, the carbonyl group attached to the α -carbon atom of the ring is reduced to a methylene group, and hydrated dihydro-deoxo-carolic (IV) and dihydro-deoxo-carolinic (V) acids respectively are formed (Clutterbuck *et al.*⁽⁵⁾).

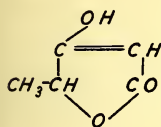
In the present communication we report on model experiments which were carried out with the object of finding suitable methods for the syntheses of these compounds.

(A) Micheel⁽¹⁰⁾ obtained monoacetone-2-carbethoxy-2-deoxy-ascorbic acid by condensing 3,4-mono-acetone-2-acetyl-1-threonylchloride with sodio ethyl malonate, and it appeared that optically active I may be prepared from sodio ethyl malonate and α -acetoxy-propionyl chloride (from optically active lactic acid) provided that racemisation did not occur in the intermediate steps, i.e. the preparation of acetyl lactic acid and α -acetoxy-propionyl chloride. The α -carbethoxy- γ -methyl-tetronic acid obtained was optically inactive. A resolution with strychnine was unsuccessful and other optically active bases will be tried.

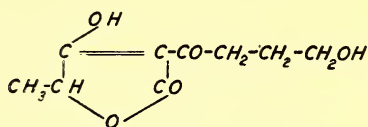
(B) It was thought that the racemic forms of IV and V could be synthesised by brominating 1-hydroxy-5-car-

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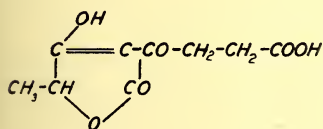
bethoxy-6-keto-octane and ethyl α -propionyl-glutarate respectively, followed by elimination of ethylbromide by a suitable treatment of the brominated products. Model



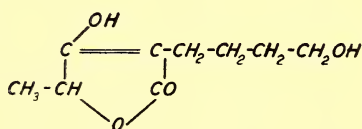
I



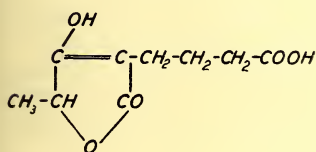
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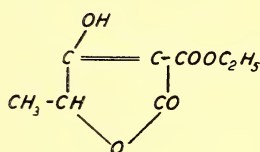
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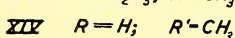
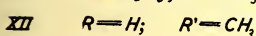
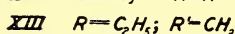
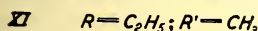
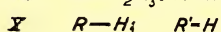
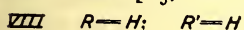
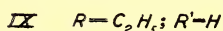
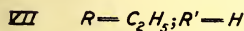
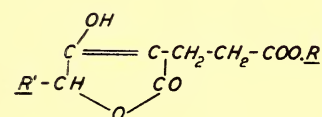
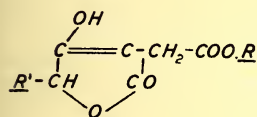
IV



V



VI



experiments have been carried out and lower homologues, VIII, X, XII, XIV, of racemic V have been synthesised. Solutions of acetyl-succinic, α -acetyl-glutaric, propionyl-succinic, and α -propionyl glutaric esters respectively in

chloroform were treated with two atoms of bromine, the intermediate bromo-derivatives were purified and ring closure was effected by carefully controlled heating *in vacuo*. The desired compounds were separated from the by-products formed by taking advantage of their solubility in aqueous sodium bicarbonate solution. The substances were obtained in good yields and in a fairly pure state. The saponification of the esters was carried out with baryta in the cold, and the free acids were obtained by the action of mineral acids on the barium salts. In continuation of this work, an attempt will be made to synthesise the racemic forms of IV and V by this method, and subsequently to resolve them.

(C) It would appear that α -carbonyl-substituted tetronic acids such as II and III could be prepared by the condensation of acid halides with the sodio derivatives of tetronic acid, analogous to the preparation of α -acyl-substituted aceto-acetic esters. It was found that solutions of tetronic acid in dry ether or dioxan did not react with sodium. An attempt was made to obtain α -acetyl-tetronic acid by adding the calculated amount of sodium ethoxide to a solution of tetronic acid in dioxan, followed by addition of acetyl chloride. Unchanged tetronic acid and sodium chloride were the only products which could be isolated from the reaction mixture.

A successful condensation in dioxan on a small scale was carried out with sodio α -carbethoxy-tetronic acid and acetyl chloride, followed by saponification and decarboxylation of the resulting product. This had a M.P. identical with that of α -acetyl-tetronic acid (79°) (Benary⁽²⁾) and did not give the violet coloration with sodium nitrite as shown by tetronic acids with a free α -position. With ferric chloride in aqueous solution an orange colour was produced, typical for α -keto-substituted tetronic acids. Mixed melting points showed that the compound was neither tetronic acid or α -carbethoxy-tetronic acid. The experiment could not be repeated when working on a larger scale. It was difficult to dissolve tetronic acid in extremely dry dioxan or ether, and no reaction could be brought about in these media. Herbert⁽¹⁰⁾ has observed that under anhydrous conditions tetronic acid and its derivatives possess the absorption bands of the keto form alone, and in these circumstances reaction with sodium is improbable. Thus the strictly anhydrous conditions under which the subsequent experiments were carried out may have been

the cause of failure. On the other hand appreciable amounts of moisture must be excluded as sodium hydroxide acts destructively on tetric acid.

EXPERIMENTAL.

Tetric Acid from α -brom-tetric Acid. Tetric acid was prepared by the method of Wolff⁽¹⁴⁾ as modified by Clutterbuck.⁽⁷⁾ It was found that the yield (30% and 32% in two experiments) of tetric acid as obtained by catalytic reduction of the α -brom-tetric acid could be increased to 48% by the addition of solid barium hydroxide (4.5 g.) to the reaction mixture (9.5 g. of α -brom-tetric acid and a catalyst prepared from charcoal (1 g.) and palladium chloride (0.2 g.)). Apparently the free hydrobromic acid formed in the reduction tends to destroy the tetric acid.

Tetric Acid from α -carbethoxy-tetric Acid. Better yields were obtained by the method of Benary,⁽¹⁾ using baryta for the saponification of the α -carbethoxy-tetric acid. The α -carbethoxy-tetric acid, obtained in 30% yield by condensing bromacetyl bromide and sodio ethyl malonate in molecular proportions, was dissolved in excess of saturated aqueous baryta solution and an almost theoretical yield of the barium salt separated after standing for a week at room temperature. The dried salt (1 g.) was ground in a mortar for 15 minutes with water (15 ml.) and the theoretical amount of N. sulphuric acid was added while grinding over a period of 30 minutes, carbon dioxide being evolved. The barium sulphate was filtered off through a thin layer of kieselguhr on filter paper, the filter cake was washed with warm water and, by allowing the combined aqueous solution to evaporate in a vacuum desiccator over sulphuric acid, tetric acid in a yield of 79% was obtained. When sodium hydroxide of the same strength was used in place of the barium hydroxide solution, a dark red substance which contained no tetric acid was obtained.

Tetric Acid from Ethyl γ -brom-aceto-acetate. This synthesis was attempted in an endeavour to obtain tetric acid in one step, eliminating the formation of α -brom-tetric acid and the subsequent reduction. Bromine ($\frac{1}{2}$ mol.) was slowly added at room temperature to a solution of ethyl aceto-acetate ($\frac{1}{2}$ mol.) in carbon disulphide (120 ml.). The mixture was washed free from hydrobromic acid after having stood overnight in the ice chest, and subsequently carefully dried over calcium chloride. (Conrad.⁽⁸⁾)

(a) Attempt to Close the Ring by Heating in Vacuo.

A portion of the dried solution was evaporated *in vacuo*. The residue (14 g.) was heated *in vacuo* (25-30 mm.) in a bath at 120° C. for 4 hours. After standing overnight, a brown solid (0.5 g.) had separated; it was filtered off and washed with benzene. The solid melted at 141°, gave the typical reactions with ferric chloride and sodium nitrite. It contained halogen and was probably a mixture of tetric acid with a brominated tetric acid. Apparently under the experimental conditions used the ethyl- γ -bromo-aceto-acetate decomposes, forming other brominated aceto-acetates which subsequently cyclise. The mother liquors and benzene washings were combined and extracted with aqueous sodium carbonate solution. When the acidified aqueous solution was extracted with ether, a solution with a blue fluorescence was obtained, and gave no colour reaction with ferric chloride or sodium nitrite.

(b) Attempt to Close the Ring by the Action of Sodium Ethoxide.

Sodium ethoxide (2 mols.) and ethyl γ -bromo-aceto-acetate (1 mol.) were brought together in a variety of solvents, leading in each case to the formation of 1,4-dicarbethoxy-2,5-diketo-*cyclo*-hexane.

Racemic α -carbethoxy- γ -methyl-tetric Acid (VI). Commercial lactic acid (242 g.) was dehydrated by heating at 60° and 25 mm. for 2½ hours. The product was cooled in ice and acetyl chloride (250 g.) was slowly added with mechanical stirring. α -Acetoxy-propionic acid (151 g.) was collected on distillation *in vacuo* (B.P. 168° at 90 mm.). α -Acetoxy-propionyl chloride was prepared by the action of purified thionyl chloride on the acid and was purified by fractional distillation (B.P. 136-138° at 14-16 mm.). The condensation with sodio ethyl malonate was carried out following the procedure of Micheel.⁽¹¹⁾ Sodio ethyl malonate prepared from sodium (20 g.) and ethyl malonate (147 g.) in ether was condensed with α -acetoxy-propionyl chloride (72 g.). After recrystallisation from ethyl alcohol, the resulting product (17.2 g.=10%) was obtained in colourless needles, melting at 88-89°. $[\alpha]_D = 0^\circ$ ($c = 0.96$ in abs. ethyl alcohol).

The strychnine salt was prepared in ethyl alcohol from equimolecular proportions of the base and α -carbethoxy- γ -methyl-tetric acid. On cooling no crystallisation

occurred. Addition of water did not induce crystallisation, and when the solvent was evaporated *in vacuo* a pale yellow gum remained. This could not be made to crystallise.

α-Carbethoxy-tetronic Acid and Phenyl-hydrazine. *α*-Carbethoxy tetronic acid may form with phenylhydrazine either a pyrazolone ($C_{11}H_8O_3N_2$) or a phenylhydrazone ($C_{13}H_{14}O_4N_2$) if steric hindrance prevents the formation of the fused two-ring system. As is shown by the results of the analysis, the phenylhydrazone is formed under the experimental conditions used. *α*-Carbethoxy-tetronic acid (1.6 g.) and phenylhydrazine (1.0 g.) were dissolved in absolute ethyl alcohol (20 ml.) and three drops of glacial acetic acid were added. The mixture was refluxed for one hour. After standing for three days at room temperature, yellow crystals melting at 152° (decomposition) were deposited. After several recrystallisations from methyl alcohol, it separated in colourless needles, M.P. 157° (dec.), which turned pink on exposure to air. Found : N=10.7% ; $C_{13}H_{14}O_4N_2$ required N=10.7%.

α-(Carbethoxy-methyl)-tetronic Acid (VII) ($C_8H_{10}O_5$). The synthesis was first effected using the methods of Ruhemann⁽¹³⁾ and of Moscheles.⁽¹²⁾ The yields obtained were very small. A synthesis with larger yields was effected as follows. Bromine (13 ml.) was added over a period of 25 minutes to a solution of ethyl aceto-succinate (49 g.) in chloroform (50 ml.). The solvent and hydrobromic acid were then removed *in vacuo*. The residual liquid was heated at $95-100^\circ$ for two working days at a pressure of 20-30 mm. A dark orange red liquid was obtained. It was dissolved in ether and the ethereal solution extracted with a saturated aqueous solution of sodium bicarbonate. The extract was washed with a little ether and concentrated hydrochloric acid added till it was acid to congo. The solution was continuously extracted with ether, the ethereal extract dried over calcium chloride, and the ether evaporated. The residual oil (14 g.) solidified on standing. After recrystallisation from benzene, colourless needles were obtained, M.P. $93-94^\circ$. An equivalent weight was determined in alcoholic solution, using phenolphthalein as indicator, a correction being made for the alcohol used. A similar procedure was used for each of the compounds subsequently described, and the results are summarised in Table I.

No.	Formula.	Mgm. Subst.	Ml. N/10 NaOH.	Equivalent.		Analyses Calculated.		Analyses Found.	
				Calc.	Found.	C.	H.	C.	H.
VII	$C_8H_{10}O_5$	75.9	4.03	186	189	—	—	—	—
VIII	$C_6H_6O_5$	118.8	15.38	79	77	45.57	3.79	45.5	3.8
IX	$C_9H_{12}O_5$	116.3	5.78	200	201	54.00	6.00	53.74	6.03
X	$C_7H_8O_5$	97.8	11.23	86	87	48.84	4.65	48.2	4.6
XI	$C_9H_{12}O_5$	462.6	22.76	200	203	—	—	—	—
XII	$C_7H_8O_5$	266.8	30.65	86	87	48.84	4.65	48.9	5.0
XIII	$C_{10}H_{14}O_5$	225.5	10.68	214	211	—	—	—	—
XIV	$C_8H_{10}O_5$	122.1	13.13	93	93	51.61	5.38	{ 51.3 51.4	{ 5.3 5.4

α -(Carboxy-methyl)-tetronic Acid (VIII) ($C_6H_6O_5$). α -(Carbethoxy-methyl)-tetronic acid (9 g.) was dissolved in saturated baryta solution (400 ml.). After standing for 5 days at room temperature, a little solid had separated, probably the barium salt. The reaction mixture was acidified with hydrochloric acid and extracted continuously with ether. An almost colourless solid separated from the ethereal extract. Colourless wing-shaped needles from anisol. M.P. 173°.

α -(β -Carbethoxy-ethyl)-tetronic Acid (IX) ($C_9H_{12}O_5$). Ethyl α -acetyl-glutarate boiling at 125°/1.7 mm. was prepared in 50% yield by the condensation of sodio ethyl aceto-acetate with ethyl β -chloro-propionate. Ethyl α -(bromacetyl)-glutarate was prepared by slowly adding bromine (3.7 ml.) to the ester (16 g.) in chloroform (40 ml.). Cyclisation was effected by heating for 10 hours to 100° at 20 mm. pressure. The reaction mixture on cooling set solid, forming a pale brown cake. It was twice recrystallised from benzene, in which it is very soluble, the mother liquors extracted with sodium bicarbonate solution and treated as described for VII, when a further quantity of the product was obtained. M.P. 78-79°.

α -(β -Carboxy-ethyl)-tetronic Acid (X) ($C_7H_8O_5$). This was prepared from IX. The same procedure was used as for VIII. Colourless needles from anisol. M.P. 175°.

α -(Carbethoxy-methyl)- γ -methyl-tetronic Acid (XI) ($C_9H_{12}O_5$). This was prepared by bromination of ethyl propionyl-succinate, followed by cyclisation (see VII). It was purified by distillation, when a pale yellow syrup was obtained; B.P. 172°/0.5 mm. It could not be made to crystallise.

α -(Carboxy-methyl)- γ -methyl-tetronic Acid (XII) ($C_7H_8O_5$). Prepared by saponification of XI (see VIII). Colourless needles from anisol. M.P. 164° .

α -(β -Carbethoxy-ethyl)- γ -methyl-tetronic Acid (XIII) ($C_{10}H_{14}O_5$). Prepared by bromination of ethyl α -propionylglutarate and subsequent cyclisation (see VII). It was purified by distillation; B.P. $190^\circ/0.45$ mm. It set partly solid on standing and was highly hygroscopic.

α -(β -Carboxy-ethyl)- γ -methyl-tetronic Acid (XIV) ($C_8H_{10}O_5$). Prepared by saponification of XIII (see VIII). Colourless needles from anisol; M.P. 134° .

α -Carbethoxy- α -acetyl-tetronic Acid (XV). α -Carbethoxy-tetronic acid (0.15 g.) was dissolved in 10 ml. of dry dioxan which had been purified according to Eigenberger⁽⁹⁾ and sodium wire (2 g.) added. A brisk evolution of hydrogen took place and white curds of the sodio derivative were formed. After standing overnight the excess sodium was removed and acetyl chloride (0.15 g.) was added. The reaction mixture became clear, and on standing sodium chloride was precipitated. After filtration, the solution was concentrated *in vacuo* and a pale yellow solid obtained. This was recrystallised from methyl alcohol; M.P. 95° , depressing the M.P. of α -carbethoxy-tetronic acid to 57° and of tetronic acid to 65° . The substance is acid to congo and gives no coloration with sodium nitrite solution.

α -Acetyl-tetronic Acid. XV was dissolved in saturated baryta (2 ml.) and the mixture warmed to 60° , when a white precipitate was formed. Sulphuric acid was added and the barium sulphate filtered off. The filtrate was extracted with ether and the ethereal extract gave no coloration with sodium nitrite solution, and gave an orange coloration with ferric chloride. After removal of the ether, a colourless crystalline substance was left; M.P. 79° , the M.P. of acetyl tetronic acid being given as 79° (Benary.⁽²⁾)

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- (5) Clutterbuck, Raistrick and Reuter : *Biochem. J.*, 1935, 29, 300.
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(¹⁴) Wolff : *Liebig's Ann.*, 1896, 291, 238.

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GRAPTOLITES OF THE GOULBURN DISTRICT,
NEW SOUTH WALES.

PART I. SOME FORMS AND LOCALITIES.

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

(With two text-figures.)

(Manuscript received, August 24, 1938. Read, October 5, 1938.)

INTRODUCTION.

Graptolites have long been known to occur in the vicinity of the Shoalhaven River, near Tallong, having been recorded by Woolnough¹ and Carne,² and subsequently described by Hall.³ The forms prescribed by Hall were apparently collected from one particular locality, and are thus not necessarily representative of the district as a whole. Hall gives the locality as "the Shoalhaven River, about nine miles from Marulan Railway Station", and it appears that they were actually found in the immediate vicinity of the Tolwong Mine, as mentioned by Carne in his earlier report. Tallong in the title of Hall's first paper is evidently a misprint for Tolwong.

For purposes of stratigraphical subdivision and correlation, collection and determination must be extended to include other localities since discovered, and the present paper is an initial step in that direction. The reference numbers given with each species enable the occurrence to be localised in conjunction with the accompanying map. The forms recorded here have been collected by the author, and for the most part determined by him. He is indebted for some of the identifications,

(¹) Woolnough, W. G. : The General Geology of Marulan and Tallong, N.S.W. *Proc. Linn. Soc. N. S. Wales*, 1909, 34, 784.

(²) Carne, J. E. : *Geol. Surv. N. S. Wales, Min. Resources*, No. 14, 1911, 346.

(³) Hall, T. S. : Notes on a Collection of Graptolites from Tallong, N.S.W. *Rec. Geol. Surv. N. S. Wales*, 1909, 8, 339; *idem* : On a further Collection of Graptolites from Tolwong, N.S.W. *Rec. Geol. Surv. N. S. Wales*, 1920, 9, 63.

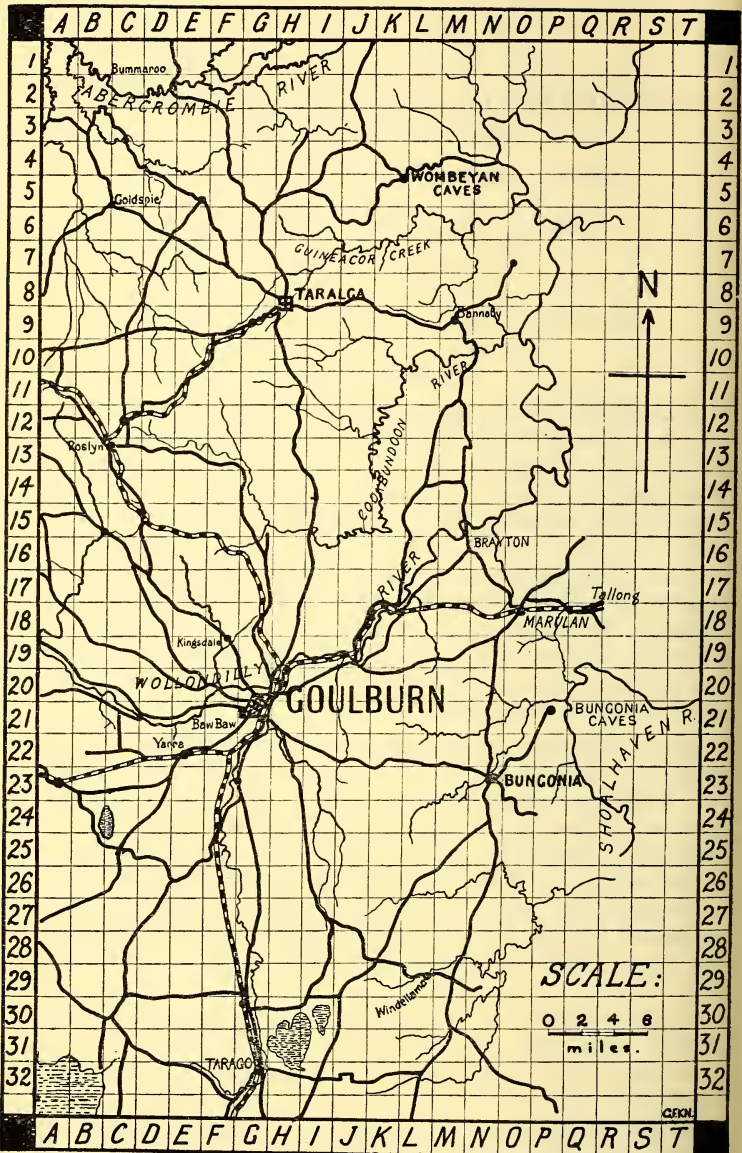


Fig. 1.

however, to Mr. D. E. Thomas, of the Geological Survey of Victoria, these being indicated in the lists by an asterisk.

While the age of the beds in which the forms occur will be indicated in broad terms, any attempt at zoning or correlation is regarded by the writer as outside the scope of this paper.

DISTRIBUTION.

The extent of the area containing the localities from which the graptolites here recorded have been collected is approximately that included in the accompanying map. No attempt has been made to show on it the geological structure, which has been indicated to some extent in the writer's earlier papers.⁴ For the purpose of recording the exact localities at which collections have been made, a grid has been superimposed upon the map. The sides of the squares of which this grid is composed are each two miles in length, and the notation adopted in the lists is based on the assumption that each square may be divided into nine smaller squares, named as shown in Fig. 2.

nw	n	ne
w	c	e
sw	s	se

Fig. 2.

Thus M16 (sw) means the south-western corner of square M16.

By this method the probable error in locating each occurrence from the map will be less than a quarter of a mile, in an area the total extent of which exceeds 2,000 square miles.

⁴ THIS JOURNAL, 1935, 69, 75-85, 123-134; 1937, 71, 45-53.

Diplograptus.—The most widely distributed and commonly occurring types belong to this genus, to which may be assigned with safety many forms not well enough preserved to enable the species to be determined. In every locality where Upper Ordovician graptolites occur, diplograptid types are usually abundant. Forms collected include :

Diplograptus spp. : C5 (w), D5 (n), D2 (e), F15 (ne), K28 (s), L11 (nw), M15 (n), M16 (c), P21 (ne), Q19 (c), Q19 (sw).

D. quadrimucronatus Hall : L22 (se), M16 (w).

D. truncatus Lapworth : K20 (nw).

D. calcaratus Lapworth : K9 (c).

D. cf. calcaratus : K20 (nw).

D. calcaratus var. *tenuicornis* Elles and Wood : K20 (nw), L22 (se), K9 (c).

Climacograptus.—Climacograpti are frequently recognizable generically amongst the scandent biserial types, though the state of preservation is rarely adequate for a specific determination. Those occurring at locality K32 (c), are however, remarkably well preserved, examination of minute thecal details being possible.

Forms collected :

Climacograptus spp. : F15 (ne), M15 (nw), M16 (w), Q19 (c).

C. scalaris Hisinger : K32 (c).

C. cf. caudatus Lapworth : J17 (se),* K32 (c).

C. supernus Elles and Wood : L19 (se).

C. rectangularis McCoy : L19 (se).

Dicellograptus.—Dicellograpti occur fairly commonly in the Upper Ordovician localities, though with less frequency than the Diplograpti or Climacograpti. Though the thecal structure in the distal portions is often obscure, the character of the proximal end and the axillary angle are usually sufficient to indicate with reasonable certainty the forms present. In some instances the structure throughout has been well preserved.

Forms collected :

Dicellograptus anceps Nicholson : E22 (c), P21 (ne).

D. divaricatus Hall : K16 (c).*

D. cf. divaricatus var. *salopiensis* Elles and Wood : L16 (se).

D. complanatus Lapworth : M16 (w).

D. cf. complanatus : K9 (c), K20 (nw).

D. cf. forchammeri Geinitz : K20 (nw), L19 (se).

Dicellograptus complanatus var. *ornatus* Elles and Wood : K9 (c).

D. sextans Hall : K16 (e).*

D. pumilus Lapworth : K32 (c), L19 (se), P22 (nw).

D. caduceus Lapworth : K15 (c).

D. cf. caduceus : P22 (ne).

D. elegans Carruthers : J17 (s), K32 (c).

Dicranograptus.—The occurrence of this genus appears to be a good deal more restricted than that of *Dicellograptus*. Moreover, it is unfortunate that in some of the localities where *Dicranograpti* are relatively abundant, the Upper Ordovician rocks in which they occur have suffered considerably from contact metamorphism. Some of the specimens collected contain chiasmolite crystals of a size nearly commensurate with the graptolites themselves, and it is hardly surprising that most of the thecal structures have been entirely obliterated. It is probable, therefore, that the genus is represented by more species than have so far been identified.

Forms collected :

Dicranograptus hians T. S. Hall : J17 (se).*

D. hians var. *apertus* : J17 (se).*

D. clingani Carruthers : J17 (se), K9 (c).

Cryptograptus.—This genus appears to be represented by only one species.

Form collected :

Cryptograptus tricornis Carruthers : J17 (se),* K16 (e).*

Leptograptus.—A few specimens of this genus, probably comprising two or three species, have so far been collected, but the details are not well preserved.

Forms collected :

Leptograptus sp. : J17 (se).*

L. cf. capillaris Carruthers : J20 (ne).

Pleurograptus.—Only one occurrence of this genus can be noted, and in this case the species is indeterminate.

Form collected :

Pleurograptus sp. : J19 (se).*

Retiograptus.—The occurrence of this genus in the district at present under consideration was first remarked by Mr. Thomas in a collection submitted to him some years ago by the writer. Since then many well preserved specimens have been collected from the same and other localities, all apparently referable to the one species.

Form collected :

Retiograpthus pulcherrimus Harris and Keble : J19 (se),*
J20 (ne), L19 (se).

Monograpthus.—Silurian rocks in three distinct localities have yielded identifiable species of this genus, while at a fourth point the writer has collected poorly preserved specimens that are only generically recognisable.

Up to the present the greatest variety has been met with in the Jerrara series near Bungonia, the forms from this locality having previously been described by the writer.⁵

Harris and Thomas,⁶ commenting on the writer's description of forms from the Jerrara series, accept the determination of *Monograpthus exiguus*, but appear doubtful as to identity of the forms referred by the writer to *M. barrandei*, *M. cf. decipiens*, *M. undulatus*, and *M. cf. tortilis*. They state: "As some of these forms are in Europe characteristic of higher or lower horizons, and have not been found in Victoria in association with *M. exiguus*, it is possible that full account has not been taken of accidents of preservation." While fully recognising the possibility of the suggestion made by the Victorian workers, especially in view of the limited number of those particular forms collected, the writer would point out that, though few, the detail in the critical cases has been fairly well preserved, and agrees closely with the descriptions given by Elles and Wood.⁷ Moreover, though not characteristic of the same horizon as *M. exiguus*, nevertheless, according to the same authority, they are occasionally found in the same zone. This would appear to be the case in the Jerrara series, where *M. exiguus* outnumbers all other types by something of the order of a hundred to one. The fact that *M. undulatus*, *M. barrandei*, *M. decipiens*, and *M. tortilis* have not been met with in Victoria, apparently not even at other horizons, is negative evidence, and does not seem to be particularly significant.

Monograpti have also been collected from the Upper Silurian strata.

⁵ The Palæozoic Sediments of Bungonia : Their Field Relations and Graptolite Fauna. THIS JOURNAL, 1935, 123-134.

⁶ Harris, W. J., and Thomas, D. E. Victorian Graptolites (New Series), Part IV. *Mining and Geological Journal*, Victorian Govt. Dept. of Mines, 1937, 1, 75.

⁷ Elles, G. L., and Wood, E. M. R. : Monograph of British Graptolites (Palæont. Soc.).

Forms collected :

- Monograptus* sp. : M19 (sw).
M. cf. decipiens Törnquist : M22 (sw).
M. undulatus Elles and Wood : M22 (sw).
M. exiguus Nicholson : M22 (sw).
M. cf. tortilis Perner : M22 (sw).
Monograptus barrandei Lapworth : M22 (sw).
M. spiralis Geinitz : M22 (sw).
M. bohemicus Barrande : J19 (s), K10 (c).
M. cf. colonus Barrande : K10 (c).
M. chimæra Barrande : K10 (c).
M. nilssoni Barrande : J19 (s).
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NOTES ON THE STRATIGRAPHY OF THE
NORTHERN TERRITORY OF AUSTRALIA,
WITH SPECIAL REFERENCE TO THE
JURASSIC SYSTEM.

By A. H. VOISEY, M.Sc.

(With Plate III and one text-figure.)

(Manuscript received, September 21, 1938. Read, October 5, 1938.)

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INTRODUCTION.

While engaged in an economic survey of certain portions of the Northern Territory in the capacity of Assistant Geologist on the staff of the Aerial Geological and Geophysical Survey of Northern Australia during 1935 and 1936, the author was able to make some observations with regard to the general geology.

The principal addition to the stratigraphy of the region is the recognition of Jurassic sediments which cover a large area. These beds, which had been called the Plateau Sandstones, were considered to be Tertiary or Cretaceous by H. Y. L. Brown, Cretaceous by Dr. W. G. Woolnough, and Permo-Carboniferous by Dr. H. I. Jensen. They

were shown as Kamilaroi beds on Professor T. W. E. David's map of the Commonwealth of Australia (David, 1932).

The map accompanying this report is based on earlier maps by Brown, Woolnough, and Jensen. Alterations have been made consistent with the author's attitude towards the age of the Plateau Sandstones. The geology of the area between the Daly and Fitzmaurice Rivers has been filled in from knowledge gained while working in that area as a member of the Survey Party. (See A.G. and G.S.N.A. Report for period ending 31st December, 1936.)

SUMMARY.

Stratigraphy.

The succession of rocks in the northern portion of the Northern Territory may be summarised as follows :

Pleistocene to Recent.

Alluvial and sandy flats, mostly flood-plains of the streams. Some areas have been reclaimed from the sea and the sediments are estuarine or marine at depth. Thicknesses variable.

Disconformity.

Tertiary.

Lateritic material and duricrust formed on the Tertiary peneplain. Thicknesses variable.

Disconformity.

Cretaceous.

Chalk-like, white, fine, granular, siliceous shales stained by iron oxide and containing *Radiolaria* and *Belemnites*. Thickness 100 feet.

Disconformity.

Jurassic.

Fine-grained siliceous shales or porcellanites, sometimes banded, containing *Otozamites bengalensis* and plant stems. Lower beds are sandstones, grits, and conglomerates, often derived from the underlying rocks. Thickness over 200 feet.

Disconformity.

Kamilaroi.

Arenaceous flaggy shales, polyzoan shales and limestones, sandstone, shale, and sand rock with marine fossils. Thickness over 700 feet.

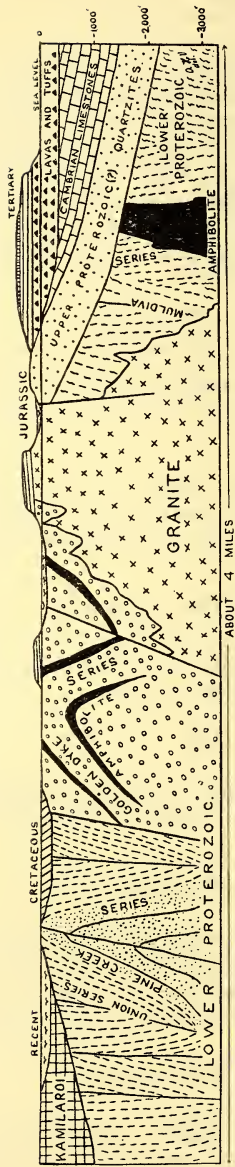


Fig. 1. Diagrammatic Section. Illustrating the Relationships between the Northern Territory Rocks.

*Disconformity.***Unknown Age.**

Dacites, andesites, calci-trachytes, dolerites, tuffs and quartzites. Thickness not determined.

*Unconformity.***Cambrian to Upper Proterozoic (?).**

Shales, calcareous shales and limestones containing *Cryptozoon* spp. and Cambrian marine fossils overlying ripple-marked quartzites. Maximum thickness not determined but certainly over 2,000 feet.

Unconformity.

Granites intrusive into Lower Proterozoic beds and introducing pegmatites and quartz reefs containing metals in places.

Lower Proterozoic.

Golden Dyke Series. Cherts, quartzites, sandstones, and graphitic slates intruded by amphibolites in the form of sills. Thickness of series at least 2,000 feet.

Pine Creek Series. Slates, sandstones, and tuffs weathering to distinctive red colours. Thickness very great but not determined.

Muldiva Series. Schists, phyllites, banded slates and quartzites possibly derived from the Pine Creek Series. Thickness not determined.

Geological Structures.

All the beds younger than Cambrian are horizontally disposed, or nearly so. The Cambrian and Upper Proterozoic (?) strata are, in some places, gently dipping but in others are folded and fractured. The Lower Proterozoic rocks are folded into basins and domes in certain localities, but generally are compressed into tight folds and have assumed vertical positions.

PREVIOUS LITERATURE.

Most of the geological pioneering work in the Northern Territory was carried out by H. Y. L. Brown and his staff, and their views are set out in numerous reports, the most relevant being listed in the bibliography. R. Etheridge, Jun., determined and described the fossils.

H. I. Jensen carried on with the work and published a number of comprehensive reports following his many visits into the field. J. E. Tenison Woods and W. G. Woolnough have contributed also to our knowledge of the area.

During the years 1935-8 the Aerial Geological and Geophysical Survey of Northern Australia has had parties of geologists and geophysicists thoroughly exploring the mining areas in order to determine their economic potentialities. Conclusions reached are published in the annual reports of the Survey for 1935 and 1936, and in a number of reports on special areas. This paper, dealing principally with areas investigated by the writer in his capacity as assistant geologist to the Survey, is intended to emphasise certain stratigraphical aspects of the work which are of little economic importance.

STRATIGRAPHY.

Pleistocene to Recent.

Alluvial flats occupy large areas of country and separate rocky hills. This alluvium has accumulated during the present cycle of erosion owing to the action of heavy monsoonal rains. Disintegrated rock material has been washed off the hills and deposited in the valleys, so that even small creeks have wide flood-plains which end abruptly against hills of almost bare rock. Watercourses wind through the alluvium but only contain running water in the wet season, during which period the whole valley is inundated frequently. For the greater part of the dry season only occasional pools of water can be found.

In metalliferous hilly country such as that around Fletcher's Gully, Buldiva, the Golden Dyke Mine, etc., creeks running through the hills have deposited gravels which have been worked for gold and tin.

Extensive plains and swamp lands such as those around the estuaries of the Victoria, Daly, Mary, and Alligator rivers were probably below sea level at one time and have since been built up and reclaimed. The topmost sediments in such cases consist of recent alluvium and wind-blown sand, but the lower beds are probably marine and estuarine sands and clays.

Tertiary.

Laterite and duricrust obscure most of the other formations between Mataranka and Daly Waters. Ridges of

ferruginous material rise above the yellow swampy soils of the Daly Waters plains and support dense lancewood and bullwaddy scrubs. Vegetation differences brought about by the variation in the soils are conspicuous.

Further north where the elevated peneplain has suffered dissection most of the laterite has been removed, but some still remains capping the table-topped hills. Brown (1906) recorded pisolitic laterite from the tablelands around the Mary River.

The laterite and duricrust were formed probably during the Tertiary era and may be correlated with the thicker and more extensive deposits further south.

Cretaceous.

The upper beds of the Cretaceous succession at Port Darwin consist of chalk-like, white, granular, siliceous shale stained in blotches by precipitated iron oxides and containing *Radiolaria* and imprints of *Belemnites*. The fossils are plentiful in a layer 12 inches thick. Where sections are best exposed the shales appear to be from 10 to 20 feet thick. They rest upon grit and conglomerate unconformably overlying Pre-Cambrian beds. It is indicated that the maximum thickness of Cretaceous beds around Darwin is less than 100 feet.

Cretaceous fossils collected from the beds were described by Etheridge (1906). These comprise *Aucella incurva* Eth. fil., *Nucula sejugata* Eth. fil., *Desmoceras carolensis* Eth. fil., *Histrichoceras antipodeus* Eth. fil., *Scaphites eruciformis* Eth. fil., *Baculites williamsoni* Eth. fil., *Baculites* sp. nov., *Crioceras* sp., *Ancyloceras?* sp., *Hamites?* *Belemnites* sp., dermal scutes, coprolites.

Brown (1906), who described the Cretaceous beds at Darwin, stated that they were typically represented by plateaux scarped seawards extending east unbrokenly to beyond Lee Point, where they dipped under more recent formations. He incorrectly regarded somewhat similar looking beds in the Pine Creek and Katherine districts as extensions of the Cretaceous strata. These were separated from the Cretaceous by Jensen (1914), who considered that all the "Plateau Sandstones" were the equivalents of the Borroloola beds, which he thought were Permo-Carboniferous. The present writer, in view of the occurrence of fossil plants, places them in the Jurassic system.

Jurassic.

The Jurassic rocks are generally found as outliers forming plateaux or table-topped hills. They are remnants of a sheet of sediments which once covered most of the area north of the Victoria and Roper Rivers. Together with some other beds, with which they have been confused, they have been described in the past as the "Plateau Sandstones".

Portion of the Tertiary peneplain was carved from these sediments, which were later uplifted, probably at the close of the Tertiary period, in blocks rising to various heights. Dissection of these strata has revealed the underlying Pre-Cambrian rocks. Nearly all the mining fields are located in valleys cut out of the plateau surface.

As the Jurassic beds are horizontal or sub-horizontal, they are unconformable with those of the Lower Proterozoic, which, commonly, are vertically disposed. In several localities, such as Katherine and Buldiva, Cambrian and/or younger rocks are interposed between these two formations.

The author has not seen Jurassic strata resting disconformably on Kamilaroi beds, but such a relationship is to be expected and may be found some day between Fletcher's Gully and Port Keats.

The continuity of these Plateau Sandstones has been recognised for many years but their age was unknown until the discovery of plant remains, namely *Otozamites bengalensis*, at Buldiva, a tin field fifty miles by track in a southerly direction from Daly River Police Station. It is inevitable, however, that, as has been the case in the past, Cretaceous, Kamilaroi, or Cambrian beds will be mapped as Plateau Sandstone in some instances where detailed work has not been carried out and where fossil remains are absent.

On the accompanying map the writer has marked as Jurassic all the rocks shown on the maps of Brown (1906, etc.) and Woolnough (1912) as Cretaceous, with the exception of a small area round Darwin. The Jurassic outcrops correspond, similarly, to the Permo-Carboniferous areas of Jensen's maps (1915), with the exception of that around Port Keats.

Although the plant remains were discovered only at one locality, there is little doubt that most of these "Plateau Sandstones" can be correlated with the Buldiva occurrence.

The Jurassic sediments were laid down upon a peneplain face of Proterozoic rocks, granites, and occasionally

Palæozoic strata. Generally the basal unit consists of sandstone with interbedded conglomerates, which are more or less abundant and discontinuous. As a result of irregularities in the surface of the peneplain the thickness of this unit is very variable. Its composition also is exceedingly diverse, and, in many cases, is dependent directly upon the underlying rock. The presence of poorly preserved plant stems and material resembling the breakdown products of the basement rocks suggests that some of the beds represent older soils which covered the land surface before inundation. Conspicuous examples of this relationship between the sediments and the underlying rocks are to be seen at the Union Hill (near Pine Creek) and in many places around Buldiva. At Union Hill the bed-rock is granite and the sediment capping the hill consists of a bedded deposit of granitic material, which passes upwards into sandstone. At Buldiva, where the sediments cover slate between Muldiva and Buldiva gorges, bands of stream tin are found among ferruginous conglomerates and sandstones. Tin-bearing pegmatite lenses occur close by and probably some are immediately beneath the deposits. Near the head of Muldiva Gorge, where the Jurassic rocks overlie granite, they consist of granite boulders, some up to four feet across, set in a matrix composed of fragments of disintegrated granite. The materials derived from the slates are not so definitely traced, but pebbles of quartzite, mostly local in origin, are found in some of the lower beds throughout the region. Concretionary sandstones follow. These spongy ferricrete rocks are generally light yellow in colour, somewhat friable in places, but more completely cemented in others. They contain limonite-filled cavities and there are indications of plant stems. These sandstones overlap the coarser basal beds in places around Buldiva, possibly owing to the uneven surface upon which the sediments were laid down.

At the Kaolin Show peculiar, vertical, pipe-like structures occur in the sandstone, giving a striking striped effect. The origin of these is not clear, but they seem to have been produced through the weathering of the rock. It is noteworthy, however, that they are confined to a bed about four feet thick which can be traced for some distance round the hill.

Above this "Tubular Sandstone" are porcellanitic, shaly, and sandy rocks which comprise the bulk of the sediments. Jensen (1919) recorded them from the Mullaman

Tableland, the Umbrawarra Hills, and Downin Tablelands, and Tenison Woods (1888) described them from other localities. At Buldiva the shale is exceedingly fine-grained and light grey in colour, weathering to white or buff. Plant remains were found by the author about 150 yards south of the "Kaolin" show on the western side of Buldiva Gorge (A.G. and G.S.N.A. Report, 1936, p. 48). They were contained in the porcellanite shed from the lower portions of the unit. The higher beds are often banded, giving rise to a spectacular rock locally known as "ribbon-stone". The bands are red to reddish-brown in colour on a white or buff background.

West of Buldiva there appear to be higher beds in the series, these being fine-grained sandstones and quartzites. Differential erosion has given rise to a distinctive terracing of the hills. The detailed sequence here was not worked out.

Although the thicknesses of the units vary considerably from point to point, the Daly River-Buldiva succession of Jurassic rocks in descending order is as follows:

	Thickness in feet.
Sandstones and quartzites (duricrust effect)	50+
White porcellanitic shales with bands of iron oxide (ribbon-stone)	10
White porcellanitic shales with <i>Otozamites</i>	20
Concretionary sandstones	20
Tin leads, conglomerates and sandstones sometimes containing plant stems ..	10-50
Maximum thickness over	150 feet

It is evident from the presence of the plant remains in the series that the beds were laid down under fresh-water conditions. Jensen (1914) justifiably disagreed from the general thesis of Tenison Woods (1888) that the white shales were of volcanic origin, but later (Jensen, 1915) recorded tuffaceous material from the lower sandy beds east of Willeroo.

Brown (1906) described rocks, certainly belonging to the Jurassic period, from the Pine Creek District and in the neighbourhood of the Mary River. He recorded a thickness of 200 feet resting unconformably on slates and arranged in the following order from top to bottom:

- (f) Concretionary and pisolitic claystone 20 feet thick.
- (e) Fine-grained white, pink and yellow sandstone.

- (d) Soft friable sandstone with flakes of mica and iron stains.
- (c) White sandstone.
- (b) Sandstone and grit with ferruginous nodules.
- (a) Conglomerate with quartzite pebbles.

He did not give further details of the thicknesses.

In another part the tableland was formed by a capping of ferruginous grit and conglomerate 30 feet thick overlying the Lower Proterozoic rocks.

Palæontological Note.

According to Walkom (1921) the genus *Otozamites* attains its widest geographical distribution in rocks of Jurassic age, but also occurs fairly abundantly in both Triassic and Lower Cretaceous formations. It has been found in Australia only in rocks of Jurassic age. The species collected at Buldiva is *Otozamites bengalensis* Oldham and Morris, and was identified by A. B. Walkom (Aerial Geological and Geophysical Survey Report, December, 1936). Dr. Walkom (1921) recorded this also from Durikai in Queensland, Mingenew, and possibly Madin-ganarra in Western Australia.

Kamilaroi.

The rocks to be discussed under this heading were described by Brown (1906) and Etheridge (1906) as "Permo-Carboniferous". It is proposed here to follow the nomenclature suggested by Professor T. W. E. David (1932) and to use the term "Kamilaroi", which, in this case, is synonymous with "Permo-Carboniferous" as used by Brown. When the matter of separation of Permian from Carboniferous rocks has been settled in other parts of the world and correlations effected with Australian sequences, the Northern Territory beds will, in all probability, be placed in the Permian System.

The Kamilaroi strata outcrop along the coast from the mouth of the Daly River to the mouth of the Victoria River but do not appear to extend far inland, as Jurassic strata or volcanic beds rest unconformably upon Lower Proterozoic or Cambrian beds east of Fletcher's Gully.

The writer has placed, tentatively, the Borooloola sandstones considered by Jensen (1915) to be Permo-Carboniferous in age, in the Jurassic system, and is not aware of any proven Kamilaroi beds other than those on the west coast within the area under review.

Brown (1906) in discussing the Kamilaroi sequence noted, at Mount Goodwin, a laminated siliceous rock associated with conglomerates and false-bedded grits. Although no alteration has been made on the map the present writer suggests the possibility of some of the upper beds of the sequence here belonging to the Jurassic suite of rocks which form the tablelands only a short distance to the west. As both systems are horizontal or nearly so, it would be difficult to determine the position of the disconformity.

Fossils were found first at Fossil Head near the mouth of the Victoria River by Commander Stokes in 1839, and they are said to be obtainable almost everywhere that a cliff section is available along this strip of coastline.

Brown (1905) states that the Fossil Head section exhibits the most typical section of the beds and is composed of strata of sandstone, shale, and sand-rock. The sandstone is micaceous and varies in texture from fine-grained to gritty. The colour is variable but is generally yellow. The sand-rock is friable, sugary, and brown. The lower beds of the section are richly fossiliferous, containing pseudomorphs in limonite of marine shells and Bryozoa. The fossiliferous portions are lenticular patches in a current-bedded matrix. The beds are almost horizontal but show a tendency to dip westwards.

Boring at Port Keats has revealed the following sequence of beds (in descending order) (Brown, 1906) :

	Feet.
Micaceous sandstones and shales with a little coal between 360 and 362 feet from the top	420
Micaceous argillaceous shale slightly carbonaceous in part and containing <i>Estheria</i>	43
Green and blue fossiliferous arenaceous shale with blue argillaceous sandstones	112
Fossiliferous polyzoan limestones	9
Sandstone	30
Pyrites and fossiliferous limestone	16
Blue sandstone, etc.	94
Black carbonaceous shale with <i>Glossopteris</i> and <i>Noeggerathiopsis</i>	6
	730

If we assume that the upper beds are Kamilaroi and that none are Jurassic it is apparent that over 700 feet of

Kamilaroi strata are present in the area. The rocks are horizontal or show a tendency to dip towards the west.

The fossils found in the Kamilaroi beds have been described by Etheridge (1906) and are as follows :

- Cyathocrinidæ* or *Platycrinidæ*.
Dybowskiella geei.
Polypora smithi.
Polypora sp.
Fenestella plebia.
Fenestella bicellulata Eth. fil.
Ramipora sp.
Rhombopora browni.
Streblotrypa browni.
Orthotetes perfidiabadensis Eth. fil.
Productus cf. *costatus*.
Chonetes cf. *pratti*.
Aulosteges baracoodensis Eth. fil.
Spirifer musakheylensis Davidson.
Chonetes sp. Fischer.
Aviculopecten ? hardmani Eth. fil.
Aviculopecten tenuicollis Dana.
? Pteronites.
? Merismopteria.
Nuculana basedowi Eth. fil.
Nuculana waterhousei Eth. fil.
Oriocrassatella stokesi Eth. fil.
Ptychomphalina humilis De Koninck.
Bellerophon costatus J. de C. Sby. var. *pennatus*.
Bucania emerii.
Pleuromutilus ? multicostatus.
Glossopteris browniana ?
Noeggerathiopsis.

Lavas and Tuffs.

Lying beneath the Jurassic sandstones which cap some of the hills south of the Daly River between Buldiva and Collia is a thin series of igneous and sedimentary rocks, which unconformably overlies the Cambrian and Proterozoic beds or rests upon the granite which intrudes the Lower Proterozoic rocks. Near Collia the basal strata are quartzites—sometimes gritty, felspathic in part, and passing upwards into tuffs. Cavities containing clusters of quartz crystals are conspicuous in these rocks. These are overlain by porphyritic lavas.

Between Collia and the Daly River these lavas rest on the quartzite, which in other places conformably underlies Cambrian limestone.

In the Victoria River area Jensen (1915) noted that similar lavas appeared to occupy erosion hollows in the Cambrian rocks. He called the volcanic suite the Victoria River Dolerite Series, and stated further that some units apparently were intrusive into the Cambrian. For this reason, he added, Brown regarded the series as Mesozoic or possibly of Tertiary age. Jensen noted further a lateritic sandstone containing what seemed to be casts of fossil wood and which he considered might be Permo-Carboniferous. As this overlay the lavas he was forced to conclude that they were post-Cambrian and pre-Permo-Carboniferous in age. However, from his description of the lateritic sandstone, it is evidently Jurassic, hence the beds are post-Cambrian and pre-Jurassic.

In further support of a post-Cambrian age for the beds it is worthy of note that the writer has not seen faulting or tilting in these beds comparable to that suffered by the Cambrian beds in the districts in which both occur. Neither have other writers recorded such effects.

Woolnough (1912) described volcanic rocks which appear to be the equivalents of those discussed above under the name of Edith River Series. Because he thought that they dipped beneath Cambrian limestones near Katherine he placed them low down in the Cambrian System. Jensen (1915) disagreed with Woolnough's observations and favoured a Permo-Carboniferous age for the series. If Woolnough (1912) is correct, there must be two volcanic series of different geological ages but possessing practically identical characteristics. Although this is unlikely, the possibility of the presence of two series must be recognised.

Jensen (1915) mentioned the Maude Creek Series of volcanic rocks, which, he said, appeared to be older than the Edith River Series.

In the Aerial Geological and Geophysical Survey's Report for 1936 the volcanic beds of the Buldiva region are referred to as the Collia Series.

It would appear that the Edith River Series, Victoria River Series, Collia Series, and, less certainly, the Maude Creek Series, are closely related to each other. The age of the lavas and their associates may be determined more satisfactorily in the Kimberley region of Western Australia,

where similar volcanic rocks occur. These are said to be intrusive into Devono-Carboniferous strata (Jensen, 1915).

Up to the present little petrological work has been done on the lavas, but this suite of dacites, andesites, calcitachytes, dolerites, and basalts showing vesicular and amygdaloidal structures is well worth detailed study.

Cambrian and Upper Proterozoic(?).

Resting upon Lower Proterozoic beds with a violent unconformity is a thick series of slightly altered sediments consisting of quartzites at the base followed by limestones with intercalated calcareous shale, shale, and sandstone bands. They are conveniently referred to in two divisions—the Buldiva Quartzites and the Daly River Limestones.

The quartzites, which must be several hundred feet in thickness, are bedded but rather uniform in their characteristics. Their colour is light reddish-brown, shading in places to purplish red where the iron content is abnormal. While the texture is generally fine, grit bands occur and one distinctive feature is the presence on some horizons of thin bands of rounded quartz pebbles. Current bedding is evident, and ripple-marks, rain prints, and sun-cracks are proof of shallow water conditions during the formation of the beds. The axes of the crests of the ripple-marks on horizons close to one another are not always parallel but are at high angles to one another, sometimes when only separated by a few inches of sediment. Bands of weathered inclusions which may have been fossils or clay galls are frequently met.

The overlying calcareous beds consist mainly of bluish-grey limestones, with other fine-grained sediments and occasional sandstones. The limestones contain abundant remains of marine fossils but these are generally fragmental and difficult to collect. More common are Cryptozoons, including *Girovanella*, which, in some places, occupy whole bands of the limestone. No measurement was made of the thickness of the limestones and their associates, but as they extend over hundreds of square miles of country and numerous beds are suggested by aerial photographs this must be considerable.

The question of the presence of volcanic rocks in the Cambrian suite has been discussed elsewhere. There does not seem to be any place for such in the Daly River-Buldiva region, and they are not mentioned by Whitehouse from Queensland or the eastern portion of the Territory.

The Buldiva Quartzites at the base of the series run from just east of Noltenius Billabong on the Daly River-Stapleton road for a distance of over sixty miles to Collia, thence southward to the Victoria River region. The relationship to the underlying Lower Proterozoic is apparently an unconformable one, but in most places where the actual junction was examined faulting was evident. Between Buldiva and Collia the quartzites are faulted against granite which intrudes the Lower Proterozoic. Limestone and its associates, possessing a general easterly dip of the order of 10° , overlie the quartzite and may be traced all the way from Noltenius Billabong to Collia. The beds are well exposed along the track from Brock's Creek to the Daly River and in the neighbourhood of Tipperary Station. The Cryptozoon bands were met about half-way between Daly River Police Station and Buldiva and again near the source of the Fish River between Buldiva and Collia. The relationships between the rocks in this area are demonstrated by the map and sections accompanying the report of the Aerial Geological and Geophysical Survey for period ending 31st December, 1936.

The limestones outcrop around Katherine and with only slight breaks in their continuity reach Queensland. In this region they have been studied principally by F. W. Whitehouse (1936). He has divided them into four series, based on the lithology, as follows:

Ninmaroo Series	Limestones.
Pituri Series	Sandstones and shales.
Georgina Series	Limestones.
Templeton Series	Sandstones and shales.

He has separated the beds also into a number of stages based on their palæontology.

Whitehouse (1936, p. 64) stated that the lowest beds of his Cambrian, the *Redlichia* Stage, at the base of the Templeton Series, rested on tilted Pre-Cambrian quartzites. He added that there has been an overlap of beds of his *Dinesus* stage in the Templeton River region.

It is apparent that the Buldiva Quartzites are absent and have been overlapped by the Templeton Series in the eastern part of the Northern Territory and in Queensland, as they can hardly be correlated with the sandstones, siltstones, cherts, and white to biscuit coloured siliceous shales. Moreover, the Templeton Series grades into limestones and is more certainly connected with the

calcareous sediments (Whitehouse, 1936). Hence it is suggested that the Daly River limestones represent parts of Whitehouse's four series. Whitehouse places his *Redlichia* stage at the top of the Lower Cambrian, so that even if we regard this stage as representing the lowest beds of the Daly River Limestones the Buldiva Quartzites are not younger than Lower Cambrian but may descend into the Upper Proterozoic. The presence in the MacDonnell Ranges of the Heavitree Quartzite which has some lithological characteristics in common with the Buldiva Quartzites and which is overlain also by *Cryptozoon* limestones suggests a comparison be made between these two sequences. Such a correlation would place all the Buldiva Quartzite in the Upper Proterozoic and would make the lowest beds of the Daly River Limestones older than the *Redlichia* stage as the MacDonnell *cryptozoon* horizon underlies the *Archæocyathinae* limestones which, in Australia, Whitehouse regards as underlying the *Redlichia* stage.

Quartzites, with purplish sandstones and shales in places, practically bridge the thousand mile gap between the Daly River and MacDonnell Range areas and, in all probability, are Upper Proterozoic or Cambrian in age. However, any correlation across such a distance must be tentative only.

Lower Proterozoic.

All of the strata underlying the Cambrian and Upper Proterozoic beds have been intensely folded and faulted. In places they have suffered metamorphism and have been changed into phyllites and low grade schists. Nowhere have they been altered to a degree comparable with the Archæozoic beds found elsewhere in the Northern Territory and in Western Australia. It would appear, therefore, that the age of these rocks must be between Archæozoic and Upper Proterozoic. They are divisible into at least three series, the Golden Dyke Series, the Pine Creek Series and the Muldiva Series. It is probable that the first named is the youngest but direct evidence is lacking. The Muldiva Series has been derived, most likely, from the Pine Creek Series but has suffered more intense metamorphism.

The Golden Dyke Series.

These beds consist of moderately altered sediments which have been intruded extensively by amphibolite

which generally took the form of sills. The sedimentary sequence in descending order in the Golden Dyke-Burrundie area consists of :

Schistose sandstones and slates.

Thinly-bedded cherts and quartzites.

Sandstones and graphitic slates.

Sandstones with interbedded conglomerates.

The total thickness of sediments here exceeds 2,000 feet. The cherts and quartzites are light grey in colour, weathering to white or grey and giving very little soil. Together with the other beds of the series they are in marked contrast to the slates of the Pine Creek Series which weather to a distinctive red colour and form an entirely different type of outcrop. The graphitic slates are conspicuous and easily followed. They contain numerous idiomorphic crystals of what appears to be chialstolite.

Conglomerate bands in the sandstone units are lenticular. The pebbles are slightly stretched owing to metamorphism but the sandstones do not show much evidence of the stresses which they have undergone.

The amphibolite seems to be associated with the Golden Dyke series and has been of great assistance in mapping the strata because, in the Golden Dyke area, it concords very closely with the bedding of the rocks. It commonly weathers more readily than the sediments and the resultant physiography is an excellent guide. Sedimentary ridges have been traversed almost continuously around the dome and basin structures in the area—the only transverse valleys being due to faulting. Three main sills of the basic rock occur in the vicinity of the Golden Dyke mine.

Pine Creek Series.

The Aerial Geological and Geophysical Survey (Report for 1935, p. 59) decided to consider the rocks in the neighbourhood of Pine Creek in two divisions, namely the Union and Pine Creek groups, the former consisting dominantly of slates and the latter of sandstones and tuffs. Because these rocks are intermingled in the Daly River area so that the division is not so well marked both groups have been combined in this paper into the Pine Creek Series.

The most distinctive and widespread rock type in the series is that known as the Union Slate. This slate is black when fresh, fissile and soft. It weathers to various

shades of red, purplish red and reddish brown. The beds owing to their incompetency have been compressed into a vertical position and outcrop as elongated ridges on which flaggy blocks of the slate protrude through the thin soil cover. These slabs are particularly susceptible to soil creep. This fact misled Brown (1906) in his interpretation of the structure. He referred to fan-folding in the Union Reefs area whereas most of the beds are vertical.

The sandstones of the "Union Group" are generally greyish-blue when fresh, soft, friable and clayey and grade into the slates.

The rocks which contain the Pine Creek gold reefs are mostly tuffs and tuffaceous sandstones some of which are quite coarse.

The fresh tuffs are black but turn to a red colour on weathering. Jensen (1919) apparently used the name of "greywacke" for unweathered tuff and "redwacke" for its weathered equivalent.

In the Daly River area belts of coarse Pine Creek tuffs sandstones and occasional conglomerates alternate with the Union slates. The conglomerates show the effect of the intense pressure to which the beds have been subjected as their contained pebbles have been stretched and flattened. These beds continue south of the Daly River and appear to pass into the more intensely altered Muldiva Series in the vicinity of Fletcher's Gully.

Muldiva Series.

These beds have been called after a gully which occurs close to Buldiva and in which the rocks are typically exposed. They outcrop, however, over most of the country between Buldiva and Fletcher's Gully and extend for an undetermined distance to the south and west of the last-named.

A great variety of rocks has been observed in this area, including low grade mica schists, knotted schists, phyllites, slates, quartzites, tuffs, sandstones, grits and conglomerates. Some of the slates are beautifully banded in black and grey colours and most possess a well marked cleavage at angles to the lamination. These are well seen in the neighbourhood of Fletcher's Gully mine. Some of the tuffs are soft, grey rocks weathering to purple and red colours while the sandstones are generally of the Pine Creek type. The schists outcrop in the creek just east of Fletcher's Gully mine and in Muldiva Gorge.

A prominent white ridge of quartzite several hundred feet high runs to the west and south of Fletcher's Gully swinging round towards Buldiva, where it is overlain by the Jurassic sandstones. This quartzite is apparently continuous with a band of partly silicified sandstones of the Pine Creek type which runs northward towards the Daly River. This and the fact that they lie on the same line of strike suggests that the Muldiva series is no more than a more intensely metamorphosed phase of the Pine Creek series.

Granites.

Granites which are intrusive into Lower Proterozoic rocks have been responsible for the introduction of pegmatites containing tin and tantalite and quartz reefs containing gold, silver, lead, wolfram, antimony, arsenic, copper and zinc.

Extensive granite outcrops occur around Pine Creek and between the Daly River-Fletcher's Gully area and the coast. Numerous other smaller occurrences have been mapped from time to time.

This granite is apparently unaffected by subsequent regional metamorphism and is similar, in a general way, to the Devonian granites of Eastern Australia, exhibiting as it does a great number of sub-types. In most cases the granite intrusions are surrounded by definite metamorphic aureoles consisting of hornfels and hardened sedimentary rock. These altered rocks are easily examined two miles to the west of Pine Creek or two miles east of the Union Reefs. In the last-named locality a hybrid rock was found on the contact near the Union Hill.

An extraordinary granite mass occurs between Buldiva and Collia. This intrusion appears to have been affected throughout by the last formed magmatic fluids, so that the feldspars have been converted into mica and the rock has the appearance of a greisen. Roof pendants of altered Lower Proterozoic schists are abundant so it is possible that this alteration may be marginal. If so it has penetrated into the parent mass to the extent of many hundreds of feet. The pegmatite and aplite veins which traverse the granite show a similar degree of alteration. Tourmaline is a characteristic constituent of the numerous pegmatite veins which, in particular, interlace the granite near its contact with the Muldiva Series.

Small pegmatite lenses in the sedimentary rocks contain the Buldiva tin oxide (A.G. and G. Survey Report, 1936).

Amphibolites.

Small bosses of amphibolite occur in the Daly River District just west of the Wheal Danks Copper Mine and about three miles to the south-west of Buldiva. In both cases the basic rock is intrusive into the Pine Creek Series. Sills of amphibolite, on the other hand, are characteristic features of the Golden Dyke Series and the writer does not know of them in any other group of rocks.

At the Golden Dyke the amphibolite has been folded with the sediments and has been intruded by granite after folding. Hence, it is older than the granite, and must have been introduced during Lower Proterozoic times.

The amphibolite is dark green in colour and exceedingly variable in texture. It gives rise to a reddish soil containing rounded weathered pebbles and generally occupies the gullies. It has been described in more detail by Jensen (1916).

GEOLOGICAL STRUCTURES.

Lower Proterozoic.

The pre-Cambrian strata of the northern portion of the Territory have been folded on approximately meridional axes. The nature of the folds has been determined largely by the composition and varying degrees of competence of the rocks.

The massive tuffs and sandstones of the Pine Creek Series type have formed anticlines and synclines which have been extensively faulted close to the axes owing to their brittleness. On the other hand, the slates and phyllites of the Union type have yielded to pressure and have been tightly compressed and overturned in places so that whenever they are found the vertical or sub-vertical position obtains. The excessive faulting which is a necessary accompaniment of such tight folding is demonstrated in areas where quartz reefs occur as these fill the fault planes. Strike faulting is most common and the zones where it is most highly developed probably represent the crests of anticlines or troughs of synclines. Dip-faults or cross-courses are present to a lesser extent but small oblique faults accompany most of the major strike faults.

Changes in pitch are indicated by the faulting in the anticlines occurring in the sandstone and tuff zones but

are completely obscured by faulting in the tightly folded slate areas.

Where there are competent arenaceous bands separated by incompetent slates as in the Daly River District these usually assume a vertical or sub-vertical position together with the slates.

The basins and domes of the Golden Dyke-Burrundie area interrupt the dominantly north-south trends and may possibly be accounted for by different and more competent sediments stiffened by the amphibolite sills which were introduced prior to the folding.

Other exceptions to the meridional strikes occur as instanced by the quartzite ranges south of Fletcher's Gully. Here again there is a difference in the competence of the beds. Faulting is prevalent and more noticeable than in the slate areas.

The granites are intrusive into the Lower Proterozoic beds and were introduced after the folding had taken place for they cut across the strike lines.

The Cambrian beds are, for the most part, gently folded, being horizontal in places, but near their boundaries with the older rocks are tilted and faulted. They are rarely steeply dipping and where folds of small amplitude occur these are in the vicinity of faults.

It is improbable that the Cambrian beds were intruded by granite in this region but the point has not been proved beyond doubt.

All the beds overlying the Cambrian are horizontal or sub-horizontal but have been seriously dislocated by block faulting, which probably occurred at the close of Tertiary times. The elevations of the plateau surfaces alter considerably between the little dissected area south of Katherine and Darwin. These differences in level are accounted for by tilting and faulting but the actual fault network has not been worked out. Several isolated faults with a small throw are located in the Buldiva-Collia region and are shown on the maps of the A.G. and G. Survey (1936). These are demonstrated by differences in the level of the units of the Jurassic which caps many of the hills.

GEOGRAPHICAL HISTORY.

A very thick series of sediments was deposited in pre-Cambrian times to the accompaniment of violent volcanic eruptions which provided beds of tuff which are intercalated

with the sediments. Amphibolite intruded the sediments in some localities, occasionally transgressing the beds, and at other times thrusting sills between them.

Then came a great diastrophic period folding the sediments and compressing some of them very tightly into anticlines and synclines. This was followed by granite intrusions.

Erosion over a long period reduced the area to a peneplain upon which sandstones, limestones and shales were laid down under marine conditions during the Cambrian period. These beds were faulted at some later time against the pre-Cambrian beds but only suffered gentle folding. Uplift and erosion followed. Volcanic activity produced tuffs and lavas of dacitic, andesitic and basaltic character which filled up erosion hollows in the land surface.

In the western region a Kamilaroi sea lapped the shores of the mainland and sediments containing abundant marine fauna were deposited.

After a long period of erosion without any important diastrophic movements practically the whole of the region under discussion was covered by a quiet fresh-water Jurassic sea. Possibly after the sediments had been uplifted and eroded off the northern areas the Cretaceous sea transgressed a portion of the land and marine sediments were laid down.

There followed a very slight uplift and a long period of quiet resulting in the formation of a Tertiary peneplain upon which laterite and clays were formed.

At the close of the Tertiary era the region was affected by block-faulting movements, which raised the various blocks to different elevations—a gradual fall being apparent northwards.

Erosion followed the uplift and the present valleys were cut out of the hills and the recent alluvial flats were formed. The coastal areas underwent the same drowning and subsequent uplift shared by the rest of Australia and the Daly River plains are the result of the reclamation of a large area from the sea.

CONCLUSION AND ACKNOWLEDGMENTS.

The main purpose of this paper has been to clarify the position with regard to the stratigraphy of the northern portion of the Northern Territory. In an attempt to generalise the writer has been forced to suggest certain correlations which may be challenged. As the work aimed

at being supplementary to other published literature, it is incomplete in itself and for a detailed study of the region the reader is referred to the bibliography appended.

In conclusion I desire to express my grateful thanks to the Director of the A.G. and G. Survey for his permission to publish these observations. I am indebted to the Senior Geologist of the Northern Territory Party, Mr. P. S. Hossfeld, and other officers of the Survey for their helpful discussions. Professor W. R. Browne of the University of Sydney and Dr. A. B. Walkom have been of great assistance to me in the preparation of this report, and to them also my thanks are due.

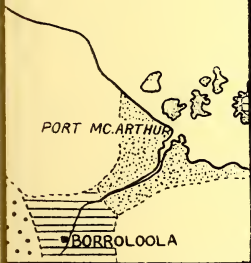
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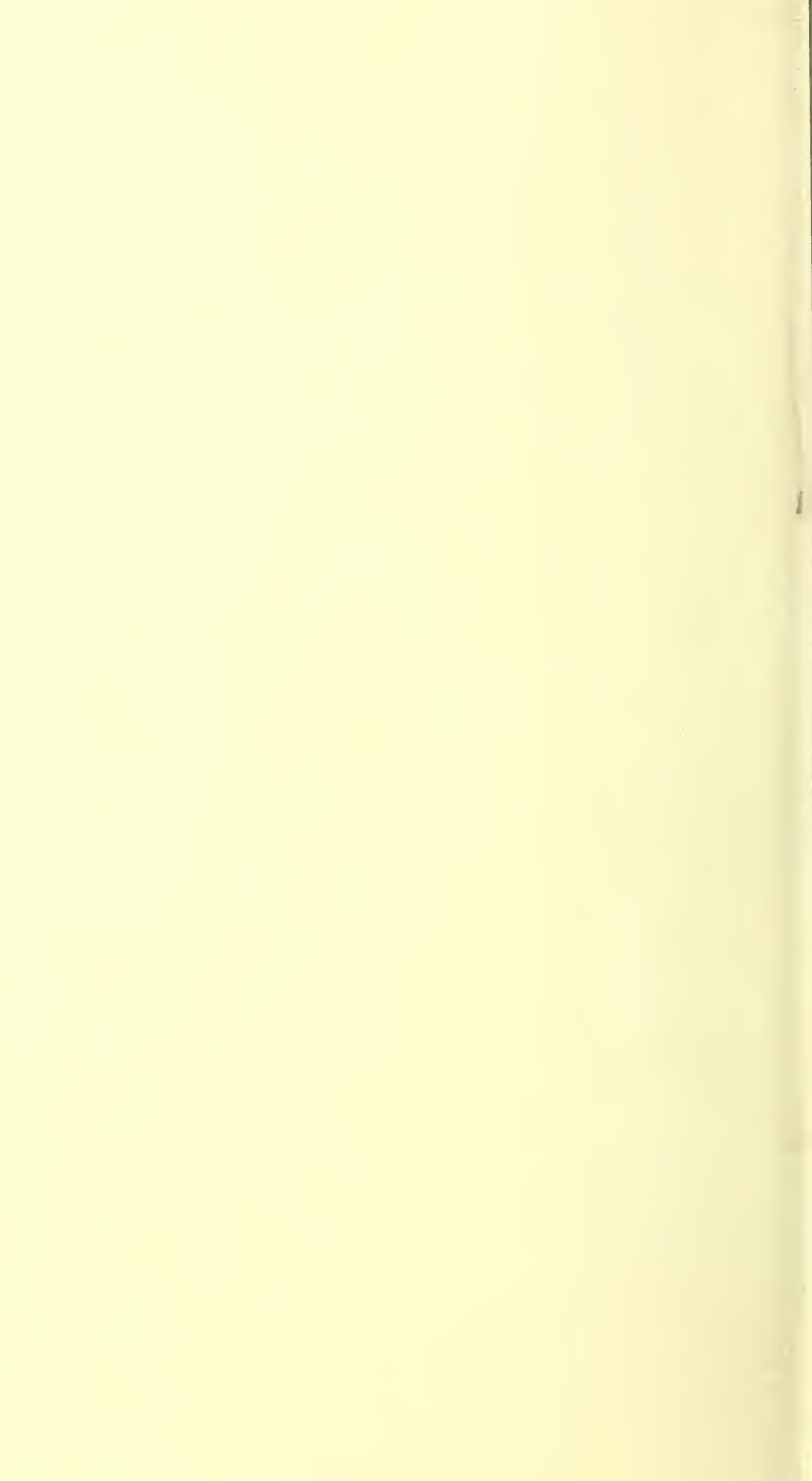
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SCALE
MILES.

20 40 60 80







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A CONTRIBUTION TO THE GEOLOGY OF THE
EASTERN MACDONNELL RANGES (CENTRAL
AUSTRALIA).

By A. H. VOISEY, M.Sc.

(With one text-figure.)

(Manuscript received, September 21, 1938. Read, October 5, 1938.)

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INTRODUCTION AND PREVIOUS LITERATURE.

There are many references in literature to the rocks of Central Australia, but most of the material has been collected by the writers during reconnaissance trips through the MacDonnell Ranges. For this reason it has fallen to the lot of each observer to revise, sometimes drastically, the conclusions of his predecessors. For example, the post-Archæozoic sequence considered by Ward (1925) to be Ordovician was subdivided later by Mawson and

Madigan (1930) into Ordovician, Cambrian, and Proterozoic beds.

Most detailed work in the Eastern MacDonnell Ranges has been carried out by Madigan and Chewings. The latter (Chewings, 1928) introduced a theme to which the present writer is unable to agree. Influenced by faulting accompanied by drag-folds in the lower beds of the Proterozoic sequence, he was led to the belief that these were much older than the overlying, comparatively little disturbed strata and separated from them by an unconformity. He considered that some of the lower beds were infolded and incorporated in the Archæozoic Arunta Complex. Chewings' views were accepted and amplified by Madigan (1932).

Ellis (1936) differed from most other observers in his avowed failure to recognise the unconformity between the basal quartzite of the Proterozoic and the Archæozoic beds. This unconformity, however, is well marked in areas which were not examined by him, and the correspondence in strike which he recorded appears to have been merely fortuitous. The quartzite beds which he observed amongst the older Archæozoic rocks were quite rightly regarded by him as belonging to that sequence, but he was misled by his acceptance of the correlations made by Chewings between these quartzites and those of the Proterozoic.

In the capacity of Assistant Geologist to the Northern Territory party of the Aerial Geological and Geophysical Survey of Northern Australia, referred to in this paper as the "Northern Australia Survey", during 1935 and 1936, the present writer was able to examine much of the structure and stratigraphy of the Eastern MacDonnell Ranges and was helped materially by aerial photographs and by a reconnaissance flight from Alice Springs to the Hale River; most of the flying and the photography were done from a height of 10,000 feet. Information relating to the geology and the economic possibilities of this area is given in the reports of the Northern Australia Survey, but the writer is indebted to the Director of the Survey for permission to publish the following additional notes.

The nomenclature of the rocks used hereafter in this paper is based on that introduced by Madigan (1932), and an acquaintance with his important work is assumed.

STRATIGRAPHY.

General Summary.

The post-Archæozoic sediments of the Eastern MacDonnell Ranges have been described in detail by Madigan (1932), and the sequence may be summarised as follows :

Ordovician.

Larapintine Series. Quartzites, calcareous and argillaceous flags, indefinite fossil moulds and worm casts.
300 feet.

Cambrian.

Pertaoorrta Series. Purple basal quartzite, massive limestones, with archæocyathinæ, conularids, algal remains.
4,100 feet.

Proterozoic.

Pertatataka Series. Calcareous and arenaceous slates and shales, dense limestones and purple shales on top.
2,030 feet.

Pertaknurra Series. Thick basal (Heavitree) quartzite, magnesian limestone, chocolate shales, massive algal limestones, calcareous and arenaceous slates. 4,600 feet.

The Pertaknurra Series rests with a violent unconformity upon gneisses, schists, greenstones, limestones, quartzites and pegmatites belonging to the Arunta Complex, which is usually regarded as being Archæozoic in age. The individual rocks of the complex are so extremely metamorphosed and recrystallised that they have very little in common with the overlying beds.

Distribution.

The distribution of the rocks is indicated in a simplified manner on the sketch-map of the Eastern MacDonnell Ranges which accompanied the report of the Northern Australia Survey for period ending 31/12/35. This map differs from that of Madigan (1932) in that a large portion of the area between Love's Creek and Winnecke shown by him as Proterozoic is included in the Arunta Complex. The White Range, Mount Gordon Range, and Paddy's Hole Range at Arltunga, and the Bald Hill-Winnecke Range are composed of quartzites and schists and are included in this extension of the Archæozoic area.

The two synclines recognised by Madigan in his Ross River Section have been completed into basin structures following aerial and ground observations.

Boundaries on the Survey's map are approximate only. The scale of the map did not permit the indication of numerous faults and folded structures which are present. Some of these are shown diagrammatically in the text figure which accompanies this report.

The Post-Archæozoic Sequence.

The writer desires to make the following comments on the interpretation of the relationships existing between the various series which Madigan (1932) has named and described.

(a) *The Larapintine Series and the Pertaoorrta Series.*

As stated by Madigan (1932, p. 97), no angular unconformity has been observed between the two series. There is a vast difference, however, in the lithology of the beds, indicating a change in the conditions of sedimentation.

(b) *The Pertaoorrta Series and the Pertatataka Series.*

The Pataknurra and Pataoorrta Series were separated from the Larapintine Series of Ward (1925) by Mawson and Madigan (1930, p. 421). They did not find any unconformity between these two new series, but regarded the Pataoorrta Series as Cambrian and the Pataknurra Series as Proterozoic on account of purple transition beds, which might be correlated with Howchin's Purple Slates in the Adelaide Series.

Excellent exposures along the Ross River show that the purple slates included in the top part of the Proterozoic contain thin bands of quartzite similar to the purple quartzite taken as the base of the Cambrian. These increase in thickness upwards until they become the main quartzite horizon.

It is recognised that there is no structural break between the Cambrian and supposed Proterozoic beds in this region.

(c) *The Pertatataka Series and the Pertaknurra Series.*

Madigan (1932, etc.) further divided the Pataknurra Series into the Pertatataka and Pertaknurra Series, having altered the spelling of the last-named to accord more closely with the aboriginal pronunciation.

He was influenced by the conclusions of Chewings (1928), who insisted on the infolding and infaulting of the Heavitree

quartzite and associated limestones with the Arunta Complex prior to the deposition of the upper beds of the sequence, and to the intrusion of the ancient granites. Such a belief forced him to separate his Pertaknurra and Pertatataka Series by "The greatest revolution that has ever affected the MacDonnells" (1932, p. 106). On the other hand, his own field work showed that the Pertatataka Series overlay the Pertaknurra Series without any apparent unconformity. The lithological relationships between both series are striking, and conformity is indicated by many sections between Undoolya Gap and Bitter Springs Gorge.

In this region Madigan accepted the most arenaceous bed in the valley, a flagstone, as the base of the Pertatataka.

The quartzite range south of the Heavitree Gap and west of the telegraph line, probably a duplication of the Heavitree quartzite, was taken by him (1933, p. 78) to represent also the base of this series. Breccias and conglomerates associated with this horizon might well be due to overthrust faulting—a point not overlooked by the same writer and Mawson in 1930 (p. 420).

The whole case for separating the Pertatataka Series from the Pertaknurra Series is based upon the mistaken correlation made by Chewings (1928) between the Heavitree quartzite and the quartzites of the White Range, Mount Gordon Range, Bald Hill-Winnecke Ranges and others. Since these quartzites were known to contain gold reefs he assumed that the Heavitree quartzite was laid down prior to the injection of Older Proterozoic auriferous granites. With the breaking down of the quartzite correlation there is no basis for the belief that the Heavitree quartzite is Older Proterozoic. On the contrary, it is not known to be invaded by granite or to contain gold. There is no need to postulate an enormous diastrophic epoch in order to mash the Pertaknurra beds into the Arunta Complex, and therefore no need to separate the Proterozoic beds into two series. Hence the present writer advocates the elimination of the name of Pertatataka Series, and suggests that the Pertaknurra Series should include the Heavitree quartzite and all the overlying beds to the base of the Pertaoorrta Series, i.e. to adopt the original divisions of Mawson and Madigan (1930).

(d) The Pertaknurra Series and the Arunta Complex.

The Heavitree quartzite at the base of the Pertaknurra Series rests, in most places, with a violent unconformity

upon the Arunta Complex. These two formations are separated by a very long time interval, and the differences in the degree of metamorphism are so great as to prevent any confusion between the rock types. Certain Archæozoic quartzite occurrences which have been correlated erroneously with the Heavitree quartzite by several workers provide an exception to the above statement. It is desirable, therefore, to cite the following differences between them :

(1) The Heavitree Quartzite is orange-yellow in colour and massive ; the Arunta quartzites are pale yellow, often white, frequently streaky and sometimes possess a parting or rough fracture corresponding to the planes of schistosity in the rocks from which they were derived.

(2) The Heavitree Quartzite is renowned for its continuity and uniformity in physical characteristics ; the Arunta quartzites are lenticular bands interbedded with gneisses and schists. They frequently grade into schists and conglomerates along their strike. Occasionally the lenses are arranged *en echelon*.

(3) The Heavitree Quartzite usually forms ranges which have a light reddish-brown appearance and are sharply defined ; the Arunta quartzites form rounded white or light-coloured hills or else, in the case of the smaller lenses, steep, sharp-topped light-coloured ridges. Viewed from the air and in aerial photographs there is rarely any doubt about the identity of the two rock types.

(4) The Heavitree Quartzite is generally found underlying limestones and lying unconformably upon the Arunta Complex ; the Arunta quartzites are associated with gneisses and schists and are on a number of different horizons. Though in the same series as altered limestones, they are rarely, if ever, in direct contact with them.

(5) No gold has been found in the Heavitree Quartzite, but it occurs in some of the Arunta quartzites, e.g. White Range, Winnecke, etc.

The Arunta Complex.

Hodge-Smith (1932) proposed a tentative classification of the Arunta Complex as follows :

- (i) The Oolgarua Acid Intrusives.
- (ii) The Everard Range Granite.

- (iii) The Ambalindum Series consisting of altered limestone and schist.
- (iv) The Augen Schist.
- (v) The Huckitta Creek Series consisting of schists and gneisses of both sedimentary and igneous origin.

Most of the rocks in the Arltunga-Claraville Gold Field probably belong to the Ambalindum Series, the Huckitta Creek Series outcropping further north in the Hart's Ranges. Hodge-Smith (p. 426) noted that the Ambalindum Series rested with marked discordance on the Huckitta Creek Series, but was doubtful whether this was really an unconformity or due to overthrust faulting. However, on this evidence he placed the Ambalindum Series tentatively in the Older Proterozoic. On the other hand, the general field evidence suggests strongly that the rocks are too intimately part of the Arunta Complex and are too intensely metamorphosed. If the discordance does indicate any time break it must be of great antiquity indeed.

The Ambalindum Series consists principally of intensely altered sedimentary rocks, some representatives being met in the White Range, which appears to be situated in an anticlinal structure pitching to the north. These consist of quartzites, quartz schists, and grey and green schists, derived respectively from conglomerates, sandstones, and mudstones. So powerful have been the stresses to which the rocks have been subjected that the pebbles in the conglomerates have been stretched in places to mere films. A bed will pass from conglomerate into a streaky quartz schist along the strike and then into quartzite. The schists separating the conglomerate bands evidently represent light-coloured sandstones. With them are the more micaceous darker rocks representing interbedded mudstones. The White Range quartzite may be followed until it passes gradually into schist. The Mount Gordon Range is composed of schist and quartzite of similar character.

Overlying the White Range rocks are knotted and micaceous schists with occasional lenticular quartzite and quartz-schist beds. It is suggested that the latter were arenaceous bands in a fine-grained succession of sediments. Occasional lenticular limestone beds have been found in this zone. Although they may not all be

in the same position in the sequence, limestones are known to occur in the following localities :

- (1) About a mile north-east of the White Range.
- (2) Fronting the Paddy's Hole Range.
- (3) About half a mile south of Arltunga Police Station.
- (4) About five miles north of the Garden Station on the River Hale.
- (5) At Winnecke just north of the main road.

These limestones are all recrystallised and contain calcite, quartz, epidote, garnet, scapolite, and sphene.

Overlying the fine-grained phase of the sequence between Jenkin's Mines and Mount Chapman are amphibolite schists separated by thin quartzite bands. The amphibolitic rocks resemble the Western Australian greenstones (Ellis, verbal communication) and may represent recrystallised tuffs. The quartzites contain felspar and alternate with the greenstones in a rhythm which varies from a fraction of an inch for each band to several feet. It is the rhythmical bedding and lack of any evidence of intrusive relationships which suggest a sedimentary origin for the rocks. In hand specimens they both appear to be igneous. Epidote is found in abundance in these beds. In addition to the greenstones and quartzites, bands of green and grey schists occur, which are similar to those underlying them.

The sedimentary series is interlaced with pegmatites and quartz reefs and is also intruded by "greenstones" similar in appearance to the so-called tuffs. The "greenstones" are often transgressive, but the pegmatites and quartz reefs concord in most places with the bedding planes, to which also the schistosity is generally parallel.

STRUCTURAL GEOLOGY.

The Post-Archæozoic Sequence.

The Post-Archæozoic sediments have been thrown into basin folds, the longer axes of which strike east and west. No corresponding domes have been found in the Eastern MacDonnell Range area. The formation of these folds has been accompanied by enormous overthrust faults, which represent adjustments in the more competent beds which failed to conform to such structures. In particular, they occur in and adjacent to the Heavitree Quartzite at the base of the sequence.

The Heavitree Range, consisting of quartzite of that name, runs eastward from the Western MacDonnell Ranges

past Alice Springs to Bitter Springs, where it ceases to be a single high ridge and breaks up into a number of hills. After branching northward it continues in an easterly direction to the Hale River.

The Heavitree Range is breached every few miles by gaps where streams have taken advantage of the faults which have broken the quartzite band. On an easterly traverse from Alice Springs these are as follows: Heavitree Gap, Emily Gap, Jessie Gap, Slip-Panel Gap, Undoolya Gap, Love's Creek Gorge, and Trepkina Creek Gorge. From the air several fractures were observed between Undoolya Gap and Love's Creek Gorge, but no streams had been able to cut through the range.

The overthrust fault followed by Trepkina Creek is a particularly important structure. The quartzite is thrown forward for about a mile and there is a magnificent development of fault-breccia between the ranges. This fault is well seen in the aerial photographs of the area and portion of it appears on page 86 of the Report of the Northern Australia Survey for 1935. Some folds in the Pertaknurra limestones are also indicated.

A similar fault, along which Love's Creek flows, has more or less isolated the quartzite between there and Trepkina Creek. A third fault on the northern side has assisted in the reversal of this huge block of rock several miles in length, and the quartzite dips northward into the Arunta Complex.

Wherever these immense overthrusts have taken place the soft overlying Pertaknurra limestones have been folded, crumpled, and faulted to an amazing degree. Recumbent folds and overfolds of every size and shape have been produced. There is little wonder that, lacking a knowledge of the overthrusts, other workers have separated such contorted beds from the comparatively undisturbed strata higher in the sequence.

The thrusting of a broken band of quartzite over a thousand feet wide for a distance of a mile into the limestones is quite a sufficient cause for all the complications which have been observed in the neighbourhood.

Several smaller areas of contortion have been observed between Undoolya Gap and Acacia Well. Some of these are associated with repetitions of the beds constituting the western end of the basin just south of Acacia Well. They involve Pertatataka as well as Pertaknurra beds. The

purple quartzite at the base of the Pertaoorra is twice repeated.

The Heavitree Quartzite does not appear immediately to the south of the basins, and is evidently deeply buried. It does not conform to the basin structures, but after changing its strike to a south-west-north-east direction for several miles it continues on its east-west strike.

The most complicated condition of the post-Archæozoic beds has occurred between Love's Creek station and Arltunga in the neighbourhood of Bitter Springs Gorge. For a distance of about ten miles along the Arltunga Road the Heavitree Quartzite and overlying limestones can be seen infolded and twisted to a remarkable extent. Fault-breccias accompany numerous flat overthrust faults. Detailed descriptions or interpretations of the structures are not possible at present, but the latter have resulted from adjustments following the concentration of pressure in this zone. The quartzite was fractured, shattered, and thrust into the limestones, rolling them ahead of it and producing the magnificent effects observed.

Proterozoic limestones have been faulted more simply against the Archæozoic schists along the western extremity of Paddy's Plain, and they are underlain by the Heavitree Quartzite, which continues with them in the direction of Winnecke. Examination of this area from a distance and from aerial photographs indicates that the quartzite then flattens and comes to rest upon the Archæozoic quartzites in the Winnecke Range. This point, however, has not been proved by field work.

A strong fault striking roughly north and south at least two miles in length and having a throw of several hundred feet was a striking feature when viewed from the air, since it dislocated the conspicuous purple quartzite band. It was located on the ground about a mile east of Acacia Well, where it has excellent physiographical expression.

The Arunta Complex.

The beds of the Arunta Complex have undergone a number of severe diastrophic epochs and have been twisted into all manner of complicated structures. The intensity of the deformation can be appreciated from the air; during a flight from Alice Springs to Arltunga, dome and basin structures associated with heavy faulting could be recognised.

A comparatively simple plunging anticline between the White Range and Claraville has permitted the investigation into the nature of the sedimentary sequence before metamorphism. Large faults, such as that which runs along Wheal Mundi Creek and continues for a distance of from ten to fifteen miles, have interrupted the succession.

Aerial photographs used by the Northern Australia Survey give valuable clues to the structures, and doubtless further details of these will be published in the Survey's reports.

TECTONICS.

The post-Archæozoic sediments were deposited in a geosyncline which covered a large area around the present position of the MacDonnell Ranges. The Archæozoic beds on which they were laid down have been elevated to form the core of an asymmetrical anticlinal structure, and constitute an easterly projection of a larger area of these rocks lying to the west. Some distance north Proterozoic deposits lie almost horizontally on the stable basement. Southward they are in a trough which has preserved a great thickness of sediments comprising Proterozoic, Cambrian, Ordovician, and perhaps Silurian beds. They have been deformed by compressive forces which were active probably during the Caledonian Epoch (Andrews, 1937).

The Heavitree Quartzite, at least 1,000 feet in thickness, is an extraordinarily competent bed overlain by about 8,000 feet of incompetent limestone beds with only about 1,000 feet of competent arenaceous beds, including the Cambrian purple quartzite 600 feet in thickness. The application of strong pressure to such a combination of beds might be expected to result in rather interesting effects and this is the case. The pressure, coming mainly from the north and south, was accompanied by components from the east and west, as is demonstrated by the basin folds. While the incompetent limestones yielded to both compressive systems, the competent Heavitree Quartzite resisted them until fracturing took place. The quartzite in contact with the Arunta Complex formed the floor of the trough and gave way in a number of places, producing overthrust faults, which are genetically related to the folds in the

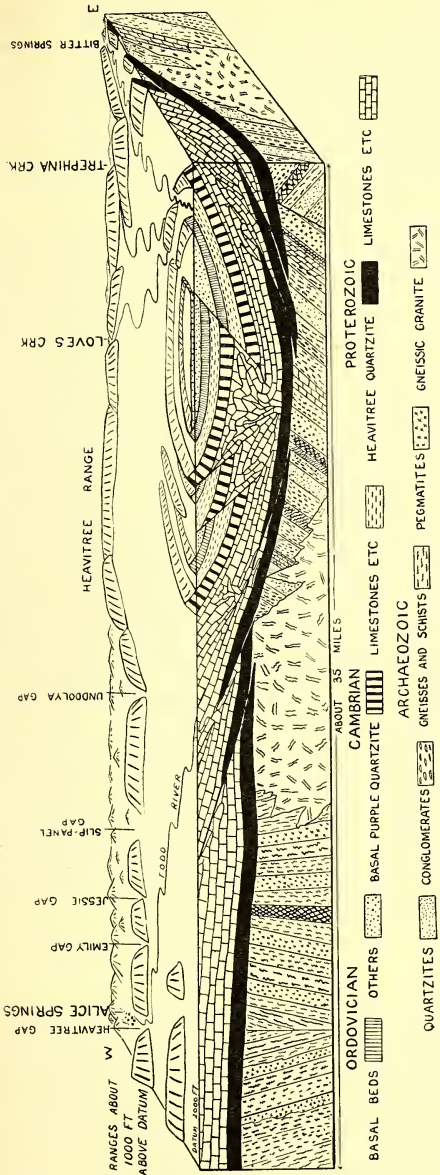


Diagram Illustrating the Sequence and Structure of the Rocks East of Alice Springs.

overlying beds. Such fracturing may well have been of similar character to the flat overthrusts seen in Bitter Springs Gorge. Pressure from north and south produced synclinal structures east of Undoolya Gap, and possibly a huge overthrust fault duplicating the Heavitree Quartzite to the west. The Quartzite bends to the north-east between the two structures in a significant manner. (See diagram and Northern Australia Survey Map, 1935.)

Pressure from the east and west was expressed in the curving upward of the beds in the synclines to form basin folds, and in the development of the magnificent set of overthrusts in quartzite of the Heavitree Range. The failure of the deeply buried quartzite to dome upwards to correspond with the basin folds necessitated adjustments involving the collapse of the beds at the western extremity of the fold and a double repetition of them by overthrusting. This faulting was accompanied by the puckering and twisting of the adjacent limestones as noted elsewhere.

While the writer is not in agreement with the conclusions reached by Chewings (1928) and Madigan (1932) with regard to the identity of certain quartzites occurring in association with the Arunta Complex, he recognises the presence in the complex of downfaulted blocks of Proterozoic strata in them. The quartzite at Simpson's Gap is an example. He opposes most strongly, however, the suggestion that any of these younger rocks have been involved in the major diastrophic epochs affecting that complex to the extent that they have been extremely altered and partly digested by it. They cannot have been intruded by auriferous granitic rocks, which are, at the youngest, Older Proterozoic in age, and which, probably, are very much more ancient.

CORRELATIONS.

If the interpretations submitted above are accepted, there is no longer any objection to the correlation of the Pertaknurra Series (including the Pertatataka) and the Nullagine Series of Western Australia, thus making it Newer Proterozoic as advocated by most writers.

The following ages and correlations are suggested for the Central Australian rocks.

Age.	Series.	Correlations.
Ordovician.	Larapintine Series.	
Cambrian to Newer Proterozoic.	<i>Possible Disconformity.</i> Pertaoorrtta Series. Pertaknurra Series.	{ Nullagine Series, W.A. { Adelaide Series, S.A. Torrowangee Series, N.S.W.
Archæozoic.	<i>Unconformity.</i> Acid and Basic Intrusives. Ambalindum Series. <i>Unconformity ?</i> Huckitta Creek Series.	Yilgarn Series, W.A. Willyama Series, N.S.W

CONCLUSION AND ACKNOWLEDGMENTS.

From the point of view of exposures few areas lend themselves so well to geological investigations as the MacDonnell Ranges. The varying responses of the beds to erosion and their distinctive colours make recognition of most horizons remarkably easy. From the air these differences are particularly well shown, and the country is splendid for aerial work. One difficulty which is met with is the lack of fences and datum points for mapping. However, this is overcome by the use of aerial photographs, and it is hoped that the excellent work initiated by the Aerial Geological and Geophysical Survey of Northern Australia will be extended at a future date to include other areas as well as those with economic possibilities.

The writer desires to express his grateful thanks to the Director of the Survey for permission to publish this work, and also to those members of the Survey staff who were his companions in the field. He is indebted to Mr. P. S. Hossfeld (Senior Geologist of the Northern Territory Party) for his introduction to the area, and for discussions on many of the ideas expressed.

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SOME COMPLEX PHTHALATES.

By GEORGE J. BURROWS, B.Sc.,
and ERNEST RITCHIE, B.Sc.

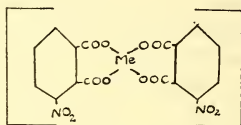
(Manuscript received, October 10, 1938. Read, November 2, 1938.)

The existence of two isomeric forms of dichloro diammine platinum led Werner (*Z. anorg. allgem. Chemie*, 1893, 3, 316) to propose a planar distribution of valences in tetravalent metals, the isomerism accordingly being of the "cis-trans" type. This hypothesis was generally accepted until 1926, when Reihlen and Nestle (*Ann.*, 1926, 447, 211) carried out molecular weight determinations of the two forms in liquid ammonia, and claimed to have found one to be dimeric. Hantzsch (*Ber.*, 1926, 59, 2761), however asserted that both forms of dichloro dipyridine platinum were monomeric in phenol. Since then numerous pairs of cis-trans isomers have been discovered, which tends to confirm Werner's original hypothesis. X-ray investigations by Cox (*J.C.S.*, 1932, 1912), Dickinson (*J.A.C.S.*, 1922, 44, 774, 2404) and others, of analogous compounds of nickel, palladium, and platinum also support these discoveries. Recently Mills and Quibell (*J.C.S.*, 1935, 839) have prepared mesostilbene diamineisobutylene diamine platinumous chloride and found that it was resolvable into a dextro and a lævo form, indicating that the valences of tetravalent platinum cannot be tetrahedrally disposed, since, if such were the case, the compound would have a plane of symmetry and would not be resolvable.

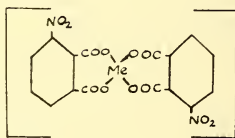
However, there is strong evidence for the tetrahedral structure. Mills and Gotts (*J.C.S.*, 1926, 3121) prepared the beryllium, copper, and zinc compounds of benzoyl pyruvic acid. The strychnine salt of the copper compound and the brucine salt of the zinc compound were found to mutarotate, whilst the beryllium compound was resolved through its brucine salt. Reihlen, Seipel and Weinbrenner (*Ann.*, 1935, 520, 256) have reported the resolution of l-a-phenylethylenediamine pyridyl platinumous salts, whilst Reihlen and Huhn (*Ann.*, 1931, 489, 42; 499, 144) claim to have resolved the bis (1,2-isobutylene diamine) platinumous

and palladous ions and the bis (2-amino methyl 3-methyl 4-ethyl quinoline) platinous, palladous, and nickel ions. Similarly platinous and palladous ions have been resolved by Rosenheim and Gerb (*Z. anorg. allgem. Chem.*, 1933, 210, 289), who used 2,3-diamino toluene as the chelate group. It is worthy of comment, however, that in no case have optically active salts been obtained after removal of the resolving agent, in these cases bromocamphor sulphuric acid.

Accordingly it was thought by the authors to be of interest to examine the complex metallic compounds of an unsymmetrically substituted dibasic acid, such as 3-nitro-phthalic acid. If the valences are planar, then cis (I) and trans (II) forms should exist, but if, on the other hand,



I



II

Me = Cu, Ni etc.

the valences are tetrahedrally disposed no such isomerism is possible, and the compound should be resolvable. It was decided to make a preliminary study of the complex phthalates.

The complex phthalates are analogous to the well known complex oxalates, but are much less stable than these. In this respect they fall roughly into three classes :

(1) Copper hydroxide and cobaltous hydroxide dissolve almost quantitatively in hot dilute sodium hydrogen phthalate, forming solutions which are stable to heat. On evaporation beautiful blue copper and purple cobalt complex salts are obtained. These salts are crystalline and quite stable in air but are readily decomposed by dilute acids and alkalis. They do not redissolve completely in

water but leave a slight residue of the simple metallic phthalate. Very dilute sodium phthalate, however, dissolves them completely.

(2) Nickel hydroxide dissolves in hot dilute sodium hydrogen phthalate nearly as readily as copper hydroxide. The resulting pale green solution is stable to heat, but on evaporation a pale green syrup is obtained, which cannot be induced to crystallise. Further evaporation in a vacuum desiccator yields a pale green solid consisting of mixed crystals of sodium phthalate and nickel phthalate, which readily redissolves in water. Apparently the complex nickel phthalate is stable in solution but breaks up into sodium and nickel phthalates just at crystallisation point. All attempts to precipitate the complex nickel phthalate as an insoluble salt were unsuccessful.

(3) Chromium hydroxide dissolves only very slightly in hot dilute sodium hydrogen phthalate, giving an olive green solution due to the formation of the complex chromiphthalate ion. Also, when excess sodium phthalate is added to a chromic salt the precipitate of chromic phthalate first formed redissolves, giving a solution of the same colour. The solutions are very unstable. On warming or concentrating, the complex breaks up, depositing chromic phthalate. Although ferric hydroxide is insoluble in sodium hydrogen phthalate, precipitated ferric phthalate redissolves in excess sodium phthalate, forming a deep reddish brown solution, showing the formation of the complex ferriphthalate ion. The complex, however, breaks up when the solution is warmed or concentrated.

Mercury, aluminium, and stannic tin show no tendency towards formation of complex phthalates.

EXPERIMENTAL.

Sodium Cupriphthalate.

Freshly prepared cupric hydroxide (from 833 grammes copper sulphate and 2.7 grammes sodium hydroxide) was added slowly to boiling sodium hydrogen phthalate solution prepared from phthalic anhydride (10 grammes), sodium hydroxide (2.7 grammes), in water (500 c.c.). After filtering off a small amount of undissolved copper hydroxide, the solution was evaporated to crystallisation and cooled. The blue crystals were filtered off, washed with a little cold water and dried in air.

Found: Cu, 13.6%; C, 37.8%; H, 2.5%.

Calculated for $\text{Na}_2[\text{C}_6\text{H}_4(\text{COO})_2\text{Cu}(\text{OOC})_2\text{C}_6\text{H}_4] \cdot 2\text{H}_2\text{O}$:
 Cu, 13.56% ; C, 38.0% ; H, 2.5%, after allowing for the
 formation of sodium carbonate in the combustion.

Sodium Cobaltophthalate.

Freshly precipitated cobalt hydroxide (from 4.76 grammes cobalt chloride and 1.6 grammes sodium hydroxide) was added slowly to boiling sodium hydrogen phthalate solution prepared from phthalic anhydride (5.92 grammes) and sodium hydroxide (1.6 grammes) in water (300 c.c.). After filtering off unchanged cobalt hydroxide, the pink solution was evaporated to crystallisation and cooled. The purple crystals were filtered off, washed with a little cold water, and dried in air.

Found : Co, 12.3% ; C, 38.8% ; H, 2.57%.

Calculated for $\text{Na}_2[\text{C}_6\text{H}_4(\text{COO})_2\text{Co}(\text{OOC})_2\text{C}_6\text{H}_4] \cdot 2\text{H}_2\text{O}$:
 Co, 12.6% ; C, 38.4% ; H, 2.56%, after allowing for the
 formation of sodium carbonate in the combustion.

ACKNOWLEDGMENT.

One of the authors (E.R.) desires to express his grateful acknowledgment to the University of Sydney for a Science Research Scholarship which enabled him to take part in this work.

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THE TORBANITES OF NEW SOUTH WALES.

PART I. THE ESSENTIAL CONSTITUENTS AND THEIR
RELATIONS TO THE PHYSICAL PROPERTIES.

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(With Plates IV, V and one text-figure.)

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INTRODUCTION.

Up till the present the study of the New South Wales torbanites, or so-called "Kerosene Shales", has been confined mainly to an investigation based on distillation tests and the results obtained from "proximate analyses". Limited microscopical examination has been carried out by palæo-botanists in conjunction with their more detailed study of the French, Scottish, and English torbanites, which are closely related to the New South Wales types. The nature of the original organic material involved in the formation of the deposits has been a subject of much controversy for many years, and even at the present time there is not complete agreement among all authorities on the subject. It is not intended that a discussion on the mode of origin of torbanite should be included in this paper, but it may be mentioned that the theory of an algal nature, first suggested for the New South Wales torbanites by

Professor David,¹ has recently gained much confirmatory evidence and is now accepted, without question, by many authorities.²

The results recorded in this paper are the outcome of a preliminary investigation in which an attempt has been made to establish a basis for the study of torbanite along the lines of coal petrology. The recognition of certain essential substances entering into its constitution, and the study of their specific properties have made possible a classification of the entities occurring in torbanite, which take the place of the macerals of coal or the minerals of an igneous rock. The present paper is mainly concerned with a description and classification of the constituents and their physical relations to the normal properties of torbanite. The results are based on a careful examination of 215 specimens collected from 25 of the principal deposits in New South Wales, and the microscopic study of 75 thin sections cut from selected specimens representing all the main types. The classification of the various torbanoid types and their relation to the canneloid materials is also being investigated.

PHYSICAL PROPERTIES.

The general appearance of torbanite is that of a compact fine-grained rock, usually of a dark greenish-brown to black colour. The fracture of the high grade varieties is typically conchoidal, but in medium to low grade material an even fracture parallel to the bedding is common. A silky or satiny lustre is present in those torbanites which possess a conchoidal fracture, and is particularly noticeable on fracture surfaces at right angles to the bedding. The conchoidal nature of the fracture is always more pronounced when the material is broken across the bedding. In this way the fracture and lustre are connected as vector properties and are controlled by the nature and orientation of certain constituents in relation to the bedding planes of the torbanite. In low-grade varieties which cleave readily along the bedding and exhibit hackly fracture the lustre is always dull. The silky lustre of torbanite is very bright in many cases, but it is quite distinct from the true resinous

¹ Notes on the Origin of "Kerosene Shale": T. W. Edgeworth David. *Proc. Linn. Soc. N. S. Wales*, 1889, 4, p. 483.

² Twenhofel: Treatise on Sedimentation, 1926, p. 299. B. N. Temperley: Botryococcus and the Algal Coals, Part II. *Trans. Roy. Soc. Edinburgh*, Pt. 3, 1935-1936, 58, p. 841.

lustre of the bright coals. In the latter the surface is very smooth and has the appearance of being extremely fine-grained, but in the torbanites it is somewhat satiny, giving the impression of a granular nature.

The specific gravity is usually low, ranging from about 1·03 to 1·35, except in the case of the siliceous torbanites, in which it rises as high as 2·00. A constant feature which distinguishes torbanite from coal and other carbonaceous material is the light colour of the streak, which varies from dark brown to light golden-yellow and greyish-white. The streak, although light coloured, is essentially dull, contrasting with the shining black streak of all normal coals and cannel coals.

Flexibility is a well-marked property of all torbanites and is accompanied by a remarkable degree of toughness in the high-grade varieties, which makes them difficult to crush. In these qualities they differ to a marked extent from coal and to a considerable extent from cannel coal. A test made on high-grade torbanite from the Hartley Vale deposit gave the following results: a test slab, 25 mm. wide and 4 mm. thick, was cut parallel to the bedding. It was supported at points 100 mm. apart and weights applied at the centre. At its breaking strain of 12·5 lbs. the slab bent through 10·5 mm. from the horizontal at the centre.

It was found that a weight, slightly less than the breaking strain, when applied as in the above test, would produce a semi-permanent curvature which remained for some time after the weight was removed, but became reduced on standing for a long period of time. A weight of 9 lbs. caused the test slab to bend through 6 mm. when first applied. After 800 hours of application the total amount of bending increased to 8·5 mm., i.e. by 41·6 per cent., and a semi-permanent curvature of 3·25 mm., or 38·2 per cent. of the total bending, was produced. This became reduced to 1·5 mm., or 17·7 per cent. on standing for 100 hours.

The results of the above test suggest that torbanite, as well as possessing considerable elasticity, is of a very slightly plastic nature capable of being deformed by pressures applied over a length of time.

Although tough and difficult to crush, torbanite is comparatively soft. Its hardness when tested according to Mohs' scale, varies from 2·25 to 2·75. The texture varies considerably in different torbanites, but it is usually

fairly homogeneous throughout any one deposit. Vertical variations seen in different degrees of lustre, and caused by fluctuations in the percentage of certain constituents, are not uncommon in a deposit but seldom give rise to definite banding.

GENERAL STRUCTURE.

When examined in thin sections, torbanite exhibits a definite microscopical structure. In general it consists of numerous, small, translucent bodies set in an opaque groundmass. Vertical sections show the translucent bodies elongated or oval in shape, lying parallel to the bedding plane (see Plate IV, Fig. 2). In horizontal sections they appear as roughly rounded masses, crowded together and separated by opaque material (see Plate IV, Fig. 1). Sections cut in intermediate directions between the bedding and the vertical show the bodies as ellipsoids, which become more elongated as the direction of section approaches the plane of the bedding. It is evident that the actual shape of the translucent bodies is that of flattened spheres. The degree of compression parallel to the bedding varies in the torbanites from different localities. In some cases the translucent bodies are much flattened, vertical sections commonly showing flat discs in which the length is twelve times that of the thickness. In other cases the length of the discs is less than six times their thickness. In the majority of the torbanites from New South Wales the ratio of length to thickness for the flattened bodies averages about nine to one.

The translucent bodies in any one specimen of torbanite show considerable variation in actual size, the greater diameter of the discs ranging from about 0.1 to 0.75 mm. in the majority of cases, but bodies with diameters as large as 1.75 mm. have been observed in some torbanites. There is usually a gradation in size between the smallest and largest of the bodies, but exceptional cases have been noted in which the bodies are set in a kind of "groundmass" formed by very small particles, producing the effect of "porphyritic grainsize". This situation suggests different types in the original organic material, or possibly two developmental phases of the same organism.

Apart from variations in the percentage and size of the translucent constituents, the microscopical structure or fabric of torbanite is remarkably uniform in both high- and low-grade types, throughout all the New South Wales

deposits. There is a complete absence of the continuous translucent laminæ which form some of the banded constituents of coal. Vertical sections of torbanite invariably show microscopical lamination on account of the parallel arrangement of the flattened bodies, and at times there is a suggestion of banding due to comparatively sharp changes in the amount of translucent material, but structurally and texturally it is essentially a non-banded substance.

PRINCIPAL CONSTITUENTS.

The various entities which occur constantly in the torbanites of the different deposits of New South Wales can be divided into two main groups depending on diaphaneity: the *translucent constituents* and the *opaque constituents*. These groups may be subdivided into specific entities which in their relation to torbanite may be regarded as equivalent to the macerals of coal or the minerals of an igneous rock. Furthermore, the nature and quality of torbanite vary as a function of the changing percentages of the essential constituents, in a manner which may be considered analogous with the variations in the igneous rock dependent upon the changing quantities of its minerals.

The translucent organically derived constituents of torbanite have been referred to by previous writers as spores, pollen grains, algal colonies, and globules of inspissated petroleum. The present paper, however, is concerned with their nature and importance in the constitution of torbanite, rather than their ancestry and derivation. It is evident that the various entities in their present state represent the changed or fossilised remains of the original organic or hydrocarbon material. It is to be hoped that subsequent research will reveal beyond all doubt the identity of the primary materials from which the macerals have been formed. Until such times as this has been attained it would seem advantageous to have names which refer to the constituent materials in their present forms.

With this object in view, a terminology has been adopted which does not necessarily involve a conception of the exact nature of the original organic material from which the entities were formed, but permits their occurrence to be studied in the torbanites from the different deposits.

The term "kerogen" was suggested by Professor Crum Brown for the material in oil-shales which gives rise to oil on destructive distillation. Although this term was

originally suggested in connection with oil-shales, it has been used by several writers in referring to the organic material of torbanites. The term kerogen is useful in referring to the hydrocarbons as distinguished from the mineral matter in the case of either oil-shale or torbanite, but it does not differentiate between the several kinds of organic bodies which exist in a normal torbanite.

The names *gelosite*, *retinosite*, and *humosite* are suggested by the writer as suitable names for three of the principal translucent constituents which are characterised by well defined properties, and the term *matrosite* is used in referring to an opaque entity. Silica is included as an essential inorganic constituent, and "jet" is described as a non-essential but frequently occurring substance.

Gelosite.

This constituent is one of the most abundant and important macerals, forming the majority of the translucent yellow discs. The name gelosite is suggested as the substance was originally referred to by Professor Bertrand as gelose or gelosic material, rich in pectic products. It occurs in all the torbanites, exhibiting physical and optical properties which remain reasonably constant, indicating a substance of a specific nature. Considered megascopically, gelosite is a yellow material which possesses a bright waxy lustre and conchoidal fracture, giving a pale yellowish-grey streak. Its hardness is in the vicinity of 2.75, and its specific gravity varies slightly within the limits of 0.95 to 1.05. When examined microscopically in thin sections, it appears as a pale yellow to yellowish-white substance which is almost transparent. It may exhibit a somewhat fibrous nature with radiating structure, but usually occurs in the form of minute rounded globules resembling organic cells, which are packed together to form the mass of most of the flattened disc-like bodies. Minute objects taking the form of tiny rod-like, or club-shaped bodies about 0.014 mm. in length often occur within the gelosite globules (see Plate IV Fig. 3). Their shape and size are fairly constant, and they usually show some regular arrangement. It has been suggested by some authorities that they represent bacteria, and they have been referred to by Renault as micrococci.³ It was suggested in 1889

³ Renault : *Bull. Soc. Ind. Minerale*, 1899, Srs. 3, XIII, pp. 1056-7.

by Professor David that they may be zoospores of gelatinous algæ,⁴ and later writers have mentioned the same possibility.

The refractive index of gelosite, which is lower than that of any of the other macerals, is reasonably constant in the torbanites from different localities. In any one specimen the actual value varies within narrow limits, but its maximum value is always lower than the minimum refractive index of the other constituents. Variations to the extent of 0·01 may occur in the same specimen, while the full range for gelosite in any of the torbanites is from 1·536 to 1·550. In the majority of cases the average refractive index lies between the limits of 1·538 and 1·545.

Anisotropism is an important property of gelosite, characterising the substance in all the New South Wales occurrences. The interference colours appear to belong to high orders, although they are masked by the natural yellow colour. Two positions of extinction and maximum illumination are exhibited in a manner similar to a doubly refracting mineral. In vertical sections the positions of extinction are parallel and at right angles to the bedding plane, maximum illumination occurring at intermediate positions. In horizontal sections the rounded disc-like bodies containing gelosite often show several centres of radiating extinction, which appear as small areas of illumination containing a dark cross, similar to a zeolite between crossed nicols. If the stage of the microscope is rotated the arms of the cross remain parallel to the vibration directions of the polariser and analyser. In horizontal sections which do not show the radiating effect, the gelosite shows a type of undulose extinction.

In addition to the normal effects of double refraction, the gelosite in a thin section of torbanite exhibits a type of "cross hatching" or rectangular arrangement of polarisation laminae. In vertical sections the laminae appear when the bedding plane makes an angle of about 27° on either side of the vibration direction of one of the nicols. The angle between the laminae and the bedding plane is about 70°. The two sets of laminae which appear on either side of the vibration direction make an angle of about 94°, as illustrated in Plate V.

The effect produced by this cross hatching somewhat resembles the twinning laminae of plagioclase felspar. Each of the elongated yellow masses in the vertical section

⁴ David : *Proc. Linn. Soc. N.S.W.*, 1889, 4, p. 500.

behaves in a similar manner during the rotation of the stage, so that all the particles of gelosite exhibit their polarisation laminæ at the one time in the same direction, giving the effect of optical continuity. This suggests that the pressure which flattened the yellow bodies parallel to the bedding of the torbanite was responsible for some form of crystallisation or internal strain in the gelosite, giving rise to the polarisation phenomena which it shows.

In sections cut parallel to the bedding plane the polarisation laminæ appear in the form of a rectangular pattern superimposed upon the radiating and undulose extinction of the gelosite. The bands are approximately at right angles, and appear brightest in a position which makes an angle of about 45° with the vibration directions of the nicols.

Anisotropism has been observed in the vitrain of several English coals.⁵ Vitrain from the "Old Coal", "Black Vein" and "Meadow Vein" of Monmouthshire exhibit extinction approximately parallel and at right angles to the bedding plane. Apart from these coals, which are stated to be of the coking metabituminous type, marked anisotropism has been observed only in anthracites, according to the reports of the English Fuel Research Board.

Retinosite.

This substance, which is present in all the New South Wales torbanites, occurs in a manner somewhat similar to gelosite, but is much less abundant. It forms small disc-like bodies which appear roughly rounded in horizontal sections and elongated in transverse sections. The particles vary in size from minute fragments to about 1.5 mm. in diameter. In selecting a name for this entity it was considered that the term retinosite would be suitable, as it indicates a substance which is not identical with gelosite, and introduces the possibility of a more resinous nature. It is not likely that the material is a true resin, but it may be a more condensed or polymerised hydrocarbon than gelosite, and perhaps allied to retinite. The colour of retinosite is essentially orange-red, and quite distinct from the pale yellow of gelosite (see Plate IV, Figs. 1 and 2). It is also less transparent, and its rounded masses seldom show the internal structures which invariably characterise

⁵ Report of the Fuel Research Board. London, March, 1936, p. 30.

the gelosite bodies. It possesses a bright resinous lustre and gives a yellowish-brown streak. The refractive index is slightly higher than that of gelosite, varying from 1.545 to about 1.558, but usually lying in the vicinity of 1.555. The specific gravity ranges from about 1.02 to 1.09, but in the majority of the torbanites it is about 1.05.

Retinosite is anisotropic, resembling gelosite in its behaviour as a doubly refracting substance. It exhibits extinction parallel and normal to the bedding plane, and frequently shows the same system of polarisation laminae as seen in gelosite, although in a number of cases this quality is absent. The retinosite bodies are usually more irregular in outline than those which consist of gelosite, and in a general way they appear to have suffered less compression. It is not uncommon to find the more angular masses of retinosite slightly protruding into the gelosite bodies, and fragments of the former have been observed embedded in gelosite, but it is probable that such cases represent "pseudo-inclusions", depending on the position in which the section is cut.

The foregoing features indicate some fundamental difference between retinosite and gelosite, and it would appear to be a generic difference rather than the result of different conditions of preservation, as the two substances often occur in contact, each well characterised by its own properties (see Plate IV, Fig. 1). It is possible that the primary material which eventually became retinosite was more susceptible to polymerisation in an environment of biochemical decay than the substance which gave rise to gelosite.

Humosite.

This substance is included among the translucent constituents of torbanite, but its nature is much more indefinite and its characters more obscure than those of gelosite and retinosite. It is almost opaque, showing a deep brownish-red colour in extremely thin sections only. It occurs without any definite habit, being distributed through the opaque matrix of the torbanite in such a way that it appears to have been moulded, to a certain extent, round the more translucent and well defined particles of gelosite and retinosite.

Between crossed nicols humosite is completely isotropic, presenting a marked contrast with the other translucent constituents. The refractive index of humosite is consider-

ably higher than in the case of the macerals already described, and appears to have a wider range, varying from a minimum of about 1.600 to as much as 1.625. Its specific gravity is also higher, and appears to be somewhat variable, ranging from about 1.15 to 1.25. The lustre is essentially dull, and the streak, as far as can be determined, is very dark brown.

The irregular masses of humosite contain no definite internal structure, but at times exhibit a somewhat granular nature. They are often crowded with minute inclusions of opaque carbonaceous material, and occasionally contain small fragments of gelosite. The general character and appearance of humosite suggests that the substance is more of the nature of a solidified ulmic or humic product of decomposition, rather than the preserved remains of more or less specific organic material.

Matrosite.

This term has been applied to a completely opaque substance which occurs as irregular particles, and forms one of the chief constituents in the opaque matrix or groundmass of torbanite. It may take the form of irregular masses more or less moulded on to the other macerals, but usually occurs as finely divided material distributed through the humosite in the groundmass and packed between the particles of gelosite and retinosite. Matrosite is usually a minor constituent but becomes more abundant in the low-grade torbanites, especially those in which the percentage of ash is high. Its specific gravity is greater than 1.45, and its streak appears to be greyish-brown.

The general nature of the substance suggests that it consists mainly of inorganic material, such as clay and fine mineral sediment which found its way into the torbanite beds during their formation. An increase of inorganic material in this form gives rise to the black "stony" torbanites of relatively high specific gravity and low volatile content, which exhibit a dark brown streak.

Jet.

A substance which resembles jet is fairly common in small quantities in torbanite. It is actually a dense, black, shining, carbonaceous substance, quite different from the torbanite, in which it occurs in the form of black shining streaks. It has been described by previous writers as closely resembling jet or in some cases gilsonite, but

possessing affinities with cannel coal.⁶ It differs in several respects from bituminous coal as shown by W. A. Dixon,⁷ who found that long fusion with caustic potash did not render it soluble in water. Its general composition is indicated in the following analyses, made on "jet" from the Joadja torbanite by the Department of Mines, Sydney (Analysis No. 3729), as quoted by Dixon⁷:

Hygroscopic moisture	1.55
Volatile hydrocarbons	40.75
Fixed carbon	55.40
Ash	2.30

The bright streaks usually lie parallel to the bedding, in which case the "jet" often represents the carbonised remains of vascular plant material such as recognisable fossils of *Glossopteris*, *Gangamopteris*, and *Phyllothea* leaves, or fragments of *Vertebraria*, occurring as extraneous material in the torbanite. These fossils, which have been observed in nearly all the New South Wales torbanites, invariably take the form of "jet", and occur interbedded in such a way that the translucent macerals of the torbanite are pressed hard against the opaque substance of the fossil fragments. The preservation of these plant remains in "jet" is important, as it indicates the fate which befalls vascular plant material which finds its way into the environment suitable for the development of torbanite.

In addition to the streaks which lie parallel to the bedding and represent fossil leaves, there also occur shining streaks of "jet" which run at random through the torbanite in all directions. This is particularly common in parts of the Newnes, Barigan, and Joadja seams. In thin sections these streaks of "jet" appear to be related to the torbanite in the same manner as the fossil leaves, but megascopic examination seldom shows any evidence of organic structure.

The important features indicated by the mode of occurrence of the "jet" which runs at random through the torbanite are:

1. That the material from which it was derived was at one time in a plastic or semi-liquid state.
2. That the torbanite, at the time of the formation of the streaks, was in a condition which would

⁶ J. E. Carne: Kerosene Shale Deposits of N.S.W. *Mem. Geol. Surv. N.S.W.*, Geol. No. 3, 1903, p. 81.

⁷ W. A. Dixon: *Rept. Austr. Assoc. Adv. Sci.*, 1887, 1, p. 137.

allow the plastic material to penetrate its mass in all directions.

3. The existing relationship between the torbanite and the "jet" suggests that the two substances were immiscible, although plastic, during the early part of the consolidation of the deposits.

It seems highly probable that the random streaks of "jet" may represent the carbonised remains of completely macerated vegetable material derived from vascular plants by extensive bio-chemical decomposition. The quantity of "jet" seldom becomes sufficiently great to influence the quality of the torbanite, and in many cases it is almost entirely absent.

Silica.

High percentages of silica are usually present in the ash of torbanites, and thin sections of the substance reveal small grains resembling quartz when examined under the microscope. It has been generally assumed that the grains of silica represent fine particles of sand introduced into the beds during the accumulation of the organic material.⁸ Grains of silica occur in all the New South Wales torbanites, abundantly in some cases and sparsely in others. It is probable that tiny grains of sand occasionally found their way into the deposits during their accumulation, but a close examination indicates that the majority of the silica, including all the larger particles, is very definitely not of simple sedimentary origin.

The particles vary in size from minute grains to two millimetres in diameter, and in quantity from about 0·05 to 25·0 per cent. of the bulk of the torbanite. The greater number of the grains are situated within the rounded gelosite bodies, usually occupying more or less central positions. The grains do not exhibit the typically rounded nature of detrital sand, nor the sharp angular shape of tuffaceous material, but take the form of irregular masses which appear to fill internal cavities in the disc-like bodies of gelosite. In vertical sections of torbanite the crystalline silica forms elongated masses lying within the flattened particles of gelosite, and actually filling the spaces which palæo-botanists consider to be the collapsed central cavities of algal colonies. In those torbanites which

⁸ J. E. Carne : The Kerosene Shale Deposits of N.S.W. *Mem. Geol. Surv. N.S.W.*, Geol. No. 3, 1903, p. 82.

contain large quantities of silica, the grains appear as large elongated masses each of which is surrounded by a layer or coat of gelosite. In horizontal sections the silica takes the form of roughly rounded masses, again situated within the gelosite bodies.

When the silica is examined between "crossed nicols" it can be seen that each mass or grain consists of numerous minute crystals moulded together so as to form a kind of crystal aggregate which takes the external shape of the gelosite body in which it is enclosed. Vertical sections through the grains usually show individual crystals of silica somewhat elongated, and arranged sub-radially within the gelosite bodies, as illustrated in Fig. 1.

In the majority of cases the crystals of silica are optically independent, extinguishing in all positions. At times,

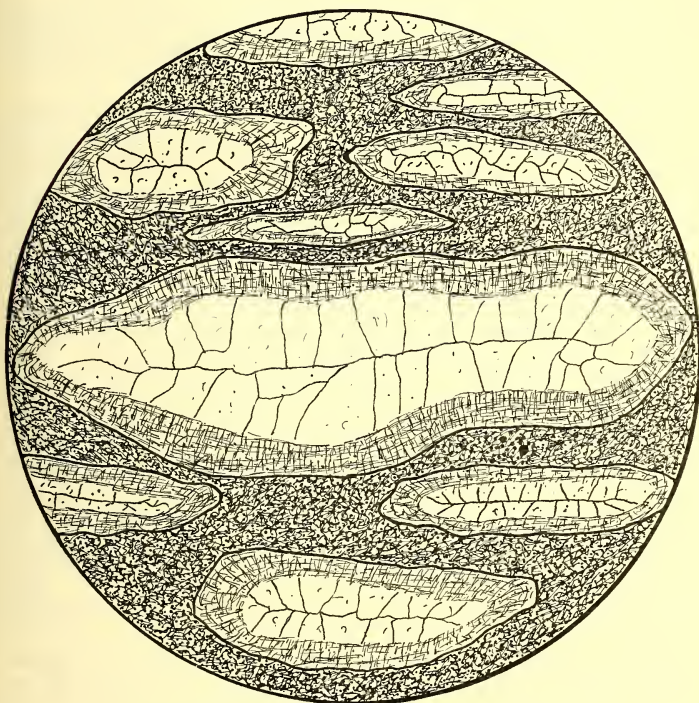


Fig. 1.—Siliceous torbanite. $\times 225$. Showing the replacement of gelosite by chalcedonic silica.

however, the crystal aggregates exhibit "radiating extinction".

The mode of occurrence and optical behaviour of the silica strongly suggest that it is in the form of chalcedony, having been deposited from solution during the development of the torbanite. The fact that it is almost invariably inclosed within gelosite suggests the deposition of silica in cavities in the gelosite bodies. Furthermore, an increase in the quantity and size of the grains is accompanied by a marked decrease in the thickness of the surrounding layers of gelosite, indicating that replacement of the gelosite by chalcedonic silica has occurred. This replacement probably followed the primary silicification which was responsible for the filling of the central cavities. The filling of open cavities in the gelosite bodies is indicated mainly by the fact that replacement commenced internally, proceeding outwards as the silicification continued. If this process of replacement had not been preceded by the deposition of silica in internal cavities, it would be difficult to understand why it should have commenced near the centres of the gelosite bodies.

It follows that the deposition of silica in open cavities must have occurred before the compression of the beds which was responsible for the flattening of the gelosite bodies. The following replacement process must have taken place after the primary compression, as is indicated by the fact that the chalcedonic silica, deposited by replacement, takes the shape of flattened gelosite bodies.

The presence of silica, deposited in the torbanite, introduces the possibility of siliceous secretion by the organisms responsible for the development of the deposits. This conception, however, is not supported by the recent investigations of Blackburn and Temperley,⁹ which show that *Botryococcus braunii*, considered to be the principal alga involved in the formation of torbanite, does not possess the power of secreting silica. It is more probable that the silicification was due to the circulation of siliceous waters through the coal measure sediments during and immediately following their deposition. These siliceous solutions may have had their origin in the large quantities of tuffaceous sediments interbedded with the coal measures.

The occurrence of rather obscure crystals in the organic matter of certain oil-shales has been noted by Dr. E. S.

⁹ Blackburn and Temperley: *Botryococcus and the Algal Coals. Trans. Roy. Soc. Edinburgh, 58, Pt. 3, 1935-1936, p. 841.*

Larsen, and W. H. Bradley has observed crystals of varying characters in the organic substance of the Green River oil shales.¹⁰

THE RELATION BETWEEN ESSENTIAL CONSTITUENTS AND PHYSICAL PROPERTIES.

The physical properties which characterise the different types of torbanite, and serve as criteria for quality, depend upon the nature and percentages as well as physical arrangement of the essential constituents. The following table illustrates the relationship which exists between the various constituents and physical properties in a number of torbanites from different localities. The specimens were selected, as far as possible, to represent the various types which occur in the Upper Coal Measures of the Kamilaroi Basin of New South Wales.

The percentages of the macerals shown in the table were estimated by a method based on the Rosiwal analysis, using the microscope and giving percentages by volume.

The light-coloured streak of torbanite is an important diagnostic property, and it is usually assumed that the highest quality types possess the lightest coloured streaks. As a general rule this is so, the light colour being due to the fact that high-grade materials contain large quantities of gelosite, which in itself possesses a pale yellowish-white streak. There are, however, several important exceptions in which the streak is light grey but the quality is very low. These are to be found among the siliceous torbanites in which replacement by chalcedonic silica has proceeded to a marked extent. An example of this type is seen in specimen No. 11, which contains only 37·5 per cent. of gelosite and 14·57 per cent. of volatile hydrocarbons, but exhibits a light grey streak. The cause of this apparent anomaly is the high percentage of replacement silica (23·4 per cent.), giving the exceptionally high ash content of 80·40 per cent. and the high specific gravity of 2·004. Similar types occur near the top of the Baerami seam and also in the thin torbanite bands associated with the Ilford seam. It follows that the specific gravity must be considered together with the colour of the streak when examining torbanites in the field.

A brownish colour in the streak is often accompanied by a fairly high percentage of fixed carbon, although there

¹⁰ Twenhofel: *Treatise on Sedimentation*, 1926, p. 299.

TABLE SHOWING THE RELATIONSHIP BETWEEN THE PERCENTAGES OF ESSENTIAL CONSTITUENTS AND THE PHYSICAL PROPERTIES OF A NUMBER OF TORBANITES FROM NEW SOUTH WALES.

Specimen No.	Locality.	Volatile Hydrocarbon %	Fixed Carbon %	Mineral Ash %	Gelostite %	Retinostite %	Replacement Silica %	Sp. Gr. Normal.	Sp. Gr. Ash-free. (Approximate).	Streak.	Lustre.	Fracture.	Colour.
1	Baerami ..	63.44	9.65	26.91	49.4	4.2	0.22	1.178	0.909	Yellowish-white.	Med. silky.	Sub. con.	Dark greenish-brown.
2	Ulan (Upper Seam)	76.72	10.72	12.56	63.4	3.1	0.18	1.110	0.984	Yellowish-brown.	Med. silky.	Sub. con.	Greenish-black.
3	Ulan (Lower Seam)	75.58	8.72	15.70	64.8	3.75	0.21	1.086	0.909	Yellowish-white.	Bright silky.	Con.	Dark greenish-brown.
4	Wollar ..	46.59	14.42	38.99	41.8	2.5	0.15	1.334	0.945	Light brown.	Dull.	Hackley.	Dark brown.
5	Wollar (Junction)	82.17	14.31	3.52	74.6	4.2	3.7	1.032	0.997	Greyish-white.	Bright silky.	Con.	Dark greenish-brown.
6	Mt. Victoria ..	59.51	19.87	20.62	50.4	6.2	1.1	1.187	0.980	Light brown.	Dull silky.	Sub. con.	Dark greenish-brown.
7	Hartley Vale ..	77.69	6.60	15.71	76.3	1.5	0.4	1.131	0.974	Light yellow.	Bright silky.	Con.	Dark greenish-brown.
8	Marrangaroo ..	68.48	7.00	24.52	68.7	2.2	0.75	1.145	0.900	Grey.	Med. silky.	Sub. con.	Dark greenish-brown.
9	Capertee North ..	55.45	20.83	23.72	60.4	4.2	0.21	1.233	0.996	Medium brown.	Dull.	Sub. con.	Dark brownish-black.
10	Capertee South ..	46.82	15.01	38.17	56.2	5.6	0.25	1.335	0.954	Medium brown.	Dull.	Hackley.	Dark brownish-black.
11	Wolgan South ..	14.60	4.97	80.43	37.5	3.4	23.4	2.004	1.200	Light grey.	Dull.	Hackley.	Greenish-grey.
12	Wolgan (Newnes)	56.08	12.27	31.65	58.3	8.2	0.18	1.239	0.923	Yellowish-brown.	Dull.	Sub. con.	Dark brownish-black.
13	Crown Ridge ..	61.96	17.42	20.62	51.5	3.4	0.30	1.182	0.976	Yellowish-brown.	Med. silky.	Sub. con.	Dark brownish-black.
14	Mornington ..	34.03	7.12	58.85	48.7	4.6	0.24	1.573	0.985	Grey.	Dull.	Hackley.	Dark brown.
15	Tong Bong Mt. ..	46.33	10.62	43.05	43.7	2.5	0.11	1.384	0.954	Light yellow.	Bright silky.	Sub. con.	Greenish-brown.
16	Genowlan (Airly) ..	54.50	23.05	22.45	41.5	1.75	0.10	1.217	0.993	Yellowish-brown.	Dull silky.	Sub. con.	Dark greenish-brown.
17	Barigan ..	59.82	10.73	29.45	47.3	5.7	1.2	1.225	0.931	Yellowish-white.	Dull.	Hackley.	Dark brown.
18	Ilford ..	60.26	9.37	30.37	41.5	4.7	13.3	1.235	0.932	Yellowish-grey.	Dull silky.	Hackley.	Dark greenish-brown.
19	Joadja ..	59.98	12.8	27.14	64.3	6.8	0.30	1.175	0.904	Yellowish-brown.	Bright silky.	Con.	Dark greenish-brown.

is no constant relationship. This is illustrated by the fact that the Wollar Junction torbanite (Specimen No. 5) possesses a greyish-white streak, although its fixed carbon content is 14·31 per cent., while the Wolgan specimen (No. 12) exhibits a yellowish-brown streak and contains 12·26 per cent. of fixed carbon. In the majority of cases, however, a brownish colour in the streak indicates a fixed carbon content of more than 14 per cent.

The specific gravity variations depend almost entirely on the amount of ash or mineral matter present in the torbanite. This relationship is illustrated by estimating the "ash-free" densities, as shown in the foregoing table. A correction which is sufficiently accurate for all practical purposes may be made by subtracting 0·01 from the normal density of the torbanite for each per cent. of ash present. The figure 0·01 is that used in making corrections for coal.¹¹

The "ash-free" densities estimated in this way are reasonably constant for all grades of torbanite, varying by no more than 0·09, which is small compared with the variation to the extent of 0·60 in the normal specific gravities. The results indicate that the density of the hydrocarbons is fairly constant. In the case of the siliceous torbanite (Specimen No. 11) the "ash-free" density is considerably greater than for the normal torbanite, and is no doubt due to the fact that the macerals of lower specific gravity, such as gelosite, were replaced in preference to the heavier humosite during silicification. It follows that the remaining hydrocarbon content in the highly silicified torbanites is heavier and of less value than the hydrocarbons in normal torbanite. This means that excessive silicification is undesirable in torbanite which is to be used in the production of oil.

The bright lustre of high-grade torbanite is essentially due to the bright resinous lustre of the maceral gelosite. As already described the lustre of torbanite is a silky or satiny sheen, which is quite distinct from the true glossy or resinous lustre exhibited by bright coals. This is due to the granular nature of the gelosite, each minute particle being surrounded by humosite or matrosite, which forms a dull groundmass.

¹¹ Strahan and Pollard: The Coals of South Wales, with Special Reference to the Origin and Distribution of Anthracite. *Mem. Geol. Surv. England and Wales*, 2nd ed., p. 12, 1915.

In the majority of the torbanites the brightness of the lustre is controlled by the amount of gelosite present, and forms an indication of quality. There are, however, several cases in which good medium quality torbanites, containing large quantities of gelosite, do not exhibit a silky lustre. Specimens Nos. 9, 10, and 12 from the Capertee and Wolgan deposits, and No. 17 from Barrigan, belong to this class. The specimen from Capertee contains 60·4 per cent. of gelosite but possesses a dull lustre, while many others, such as Nos. 6, 13, 16, and 17, containing less gelosite, show silky sheens, and No. 15, from Tong Bong Mountain, containing only 43·7 per cent. of gelosite, exhibits a bright silky lustre. These anomalies occur among the medium-grade torbanites, in which the percentage of gelosite lies between about 40 and 60. Any material containing over 60 per cent. invariably exhibits a silky lustre, and those with less than 40 per cent. always show a dull surface. It is evident in the case of the medium-grade torbanites that the quality is related more closely to the percentage of gelosite than the degree of lustre, which means that the latter property cannot always be relied upon as an exact guide to quality.

The lustre of the silky torbanites is always brightest on fracture surfaces which lie more or less at right angles to the bedding plane. This relationship between the direction of fracture and the brightness of lustre is due to the fact that the particles of gelosite are much flattened parallel to the bedding. When a fracture occurs in this direction the material tends to cleave between the flattened gelosite bodies which remain covered with thin films of the dull groundmass on the resulting surface. When a fracture takes place across the bedding, the gelosite bodies are broken and their bright lustre is exposed on the surface. It is probable that the absence of lustre in some of the torbanites which contain up to 60 per cent. of gelosite is due to a groundmass which is sufficiently soft to allow fracturing to occur in all directions without breaking the gelosite bodies.

The typical conchoidal fracture of high-grade torbanite is also closely connected with the amount of gelosite present, and is usually associated with silky lustre. The cause of this fracture seems to be due to homogeneity in the torbanite resulting from the close packing of the gelosite bodies, each of which tends to fracture in a conchoidal manner. The fracture is always more conchoidal on surfaces which

are transversely opposed to the bedding plane. This is due to the same cause which produces variations in the silky lustre on surfaces along different directions, namely the tendency to cleave without breaking the gelosite bodies when fractured parallel to the bedding plane.

The natural colours of torbanite are confined mainly to dark greenish-brown, dark brown, and black. Some of the siliceous types possess lighter shades of green and brown, becoming greenish-grey when the amount of replacement silica is above 20 per cent. The very dark colours of the normal types are due to the deep brown or almost black colour of the humosite which incloses each of the golden yellow gelosite bodies. The deep brown of the humosite is no doubt a result of the brown staining effect of humic products of decomposition.

The colour of torbanite is always much darker on surfaces more or less parallel to the bedding. This is again linked up with the fact that fracturing in such directions does not expose the yellow of the gelosite on the surface.

The different colours of torbanite indicate types rather than qualities. The highly siliceous types are green or greenish-grey. Those with silky lustre and conchoidal fracture are usually greenish-brown, while the better grade types with dull lustre are dark-brown and the low quality materials black.

The flexibility and toughness of the higher grade torbanites seems to be a result of similar properties in the gelosite. This is indicated by the fact that the foregoing properties become more marked as the percentage of gelosite increases. The more brittle nature of low-grade torbanite suggests that the humosite and matrosite of the groundmass lack flexibility. In the high-grade material, these substances form no more than thin films separating the gelosite bodies, and consequently permit the toughness and flexibility of the gelosite to influence the nature of the torbanite as a whole.

ACKNOWLEDGMENTS.

In conclusion the writer wishes to acknowledge that the commencement of an investigation into the torbanites of New South Wales, the results of which are recorded in this paper, was made possible by the Deas Thompson Scholarship and also facilities provided by the Department of Geology, University of Sydney.

EXPLANATION OF PLATES.

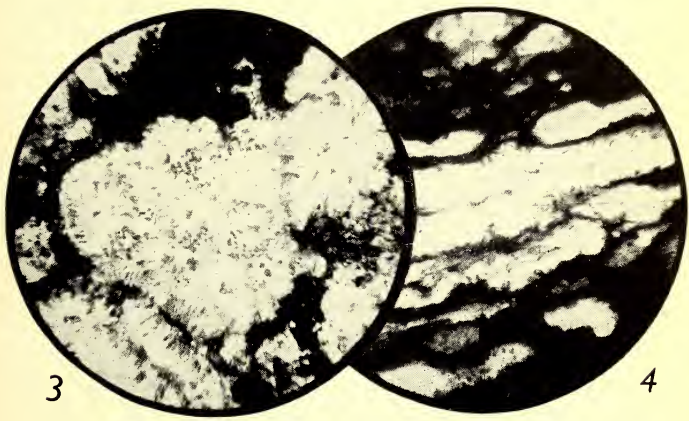
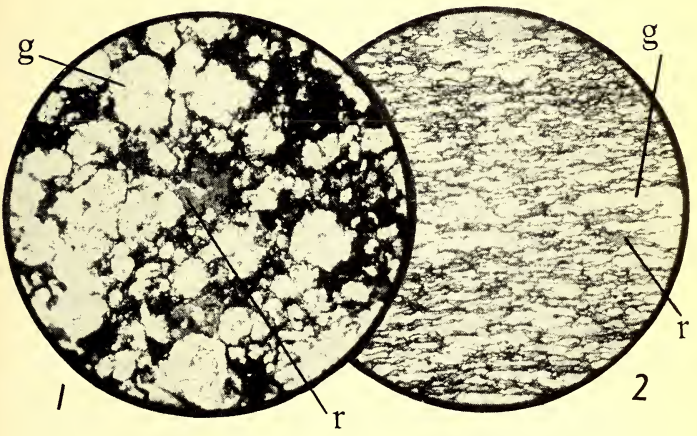
PLATE IV.

Photomicrographs of Torbanite from the Baerami Deposit.

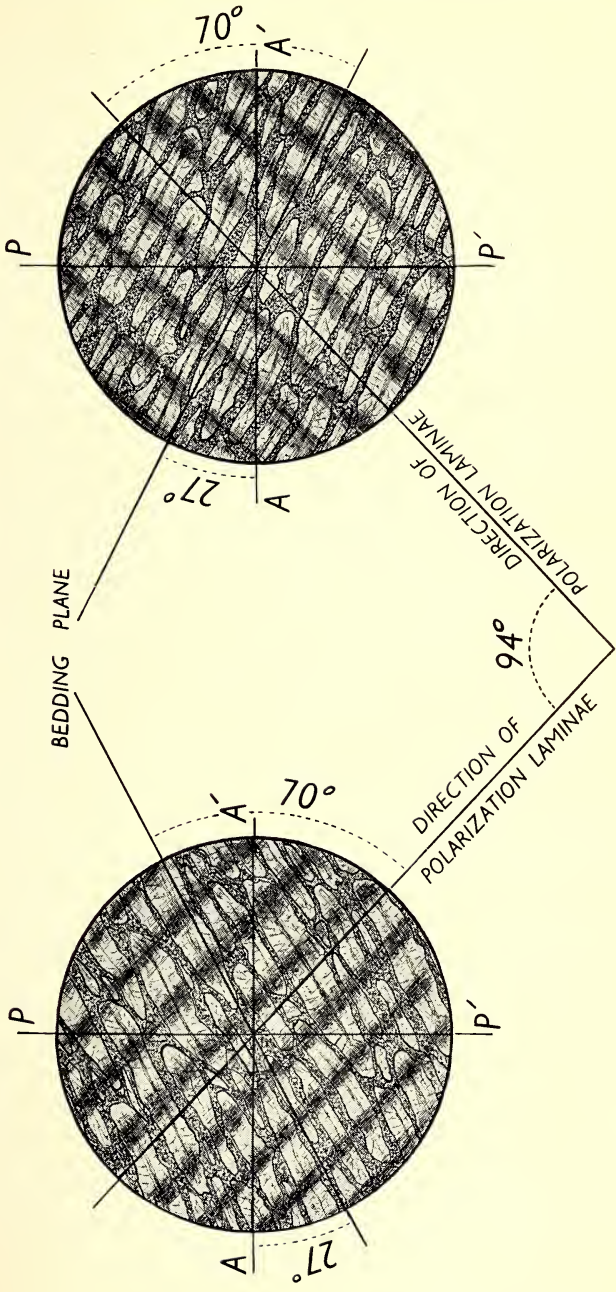
1. Horizontal section, 30 diams. Showing rounded masses of gelosite (*g*), set in an opaque groundmass of humosite and matrosite. A small particle of retinosite (*r*), can be seen near the centre of the photograph, appearing much darker than the gelosite.
2. Vertical section, 30 diams. Showing flattened masses of gelosite and opaque matrix. Several flattened particles of retinosite (*r*) can be seen on the right-hand side of the photograph.
3. Horizontal section, 150 diams. Showing a particle of gelosite, which occupies most of the field, containing minute club-shaped bodies. The groundmass appears opaque in this section.
4. Vertical section, 150 diams. A transverse section of a particle of gelosite similar to that shown in Fig. 3. The collapsed central cavity of the mass can be seen near the centre of the photograph.

PLATE V.

A vertical section of torbanite in two positions between crossed nicols, illustrating the two sets of polarisation laminæ.









PRELIMINARY NOTE ON THE NATURE OF THE STRESSES INVOLVED IN THE LATE PALÆOZOIC DIASTROPHISM IN NEW SOUTH WALES.

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and G. D. OSBORNE, D.Sc.

(*Manuscript received, October 19, 1938. Read, November 2, 1938.*)

INTRODUCTION.

The conception has gradually emerged from regional studies by many workers on the structural geology of the Upper Palæozoic rocks of eastern Australia that a coastal belt extending from the Hunter Valley in the south for about a thousand miles in a general north-north-westerly direction to beyond Townsville, after receiving considerable thicknesses of Upper Palæozoic sediments, was folded and faulted and injected by granitic batholiths during an important diastrophic epoch of late Palæozoic age. In a recent paper (Carey and Browne, 1938) this diastrophism was called the Hunter-Bowen orogeny.

Along the western margin of the folded zone in N. S. Wales the dominant structure is a great thrust line, which may best be described as the Hunter-Mooki System. This comprises (*a*) in the south the Hunter Thrust and associated structures, the dominant features of which were described by Osborne (1929, pp. 444-50), and (*b*) in the north the Mooki Thrusts of the Werrie Basin described by Carey (1934*a*, pp. 362-5). The former author had taken the view that the development of the great boundary thrust-system took place during crustal movement distinctly later than the general folding and faulting of the Upper Palæozoic rocks of the Hunter River District, while the latter considered that the Mooki thrusts were genetically connected with the development of the folded tract.

In recent years regional mapping of the Carboniferous and Devonian rocks of the Upper Hunter, Upper Manning, and Stroud-Bulahdelah-Gloucester districts has been carried out by one of us (see Osborne, 1937). A consideration of the patterns of the faults and the arrangements of the great

thrusts and serpentine lines in these areas, together with the data from the Scone-Maitland belt, has now convinced that author that the Hunter Thrust System is to be placed among the late Palæozoic structures, although it must still be emphasised that a considerable amount of deformation, with folding and normal faulting, had proceeded before the development of the major peripheral thrusts.

In the past it has been assumed that all the folds and faults were produced by simple compression, and that systems of intersecting faults had been generated by successive earth movements operating in differing directions. Further, closed structures, some with curving axes, were regarded as due to cross folding. The purpose of the present note is to give preliminary announcement of the recognition of the fact that important shearing and torsional elements, accompanied by conjugate tension and compression, have contributed largely to the tectonic evolution of the late Palæozoic orogen.

MECHANICS OF SHEARING.

Before summarising some of the evidence to support the view stated in the latter part of the last paragraph, let us review briefly the fundamental principles of shearing deformation.

The Strain Rhomb.

Consider a square column of rock which is being deformed by a horizontal shearing stress. The internal stresses set up within a section in the plane of the shear are shown in Fig. 1. One diagonal of the square is shortened, the other is lengthened. The stresses in the vertical plane of the shortest diagonal are entirely compressional. If relief is by folding, the fold axes will tend to be at right angles to the shortened diagonal. The stresses in the vertical plane of the lengthened diagonal are entirely tensional, and tension fractures will tend to form at right angles to this diagonal. The strain pattern, then, of a square area of the earth's surface deformed under such a shear system may be a series of folds oblique to the stress with a cognate series of tension faults transverse to the folds (Fig. 2). If failure is by shear fractures instead of folding, the strain system will be as shown in Fig. 3. These figures may be combined into a single diagram, Fig. 4, which depicts in azimuth and sense all the possible resultant structures which may originate from the given impressed shearing

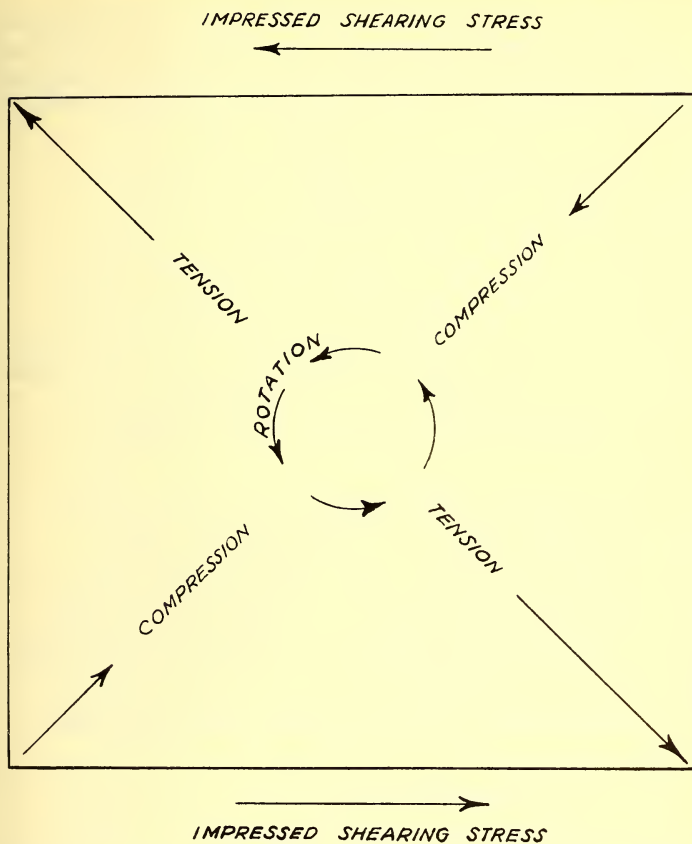


Fig. 1.—Internal stresses set up in square section by impressed shear.

stress. In general, all of these structures will not be found in one zone deformed by shearing stress. The elastic nature and load environment of the rocks deformed will decide which of these structures will develop.

In a region of relatively rigid and competent rocks we may expect a lozenge-shaped system of conjugate shear-thrusts to dominate the pattern. In such cases the strike of the sediments involved in the fault blocks may be aligned parallel to the direction of compression, or if the materials are sufficiently rigid the relief of the stress may be solely by shearing. In the upper part of a thick sedimentary series of no great competence, moderate shearing deforma-

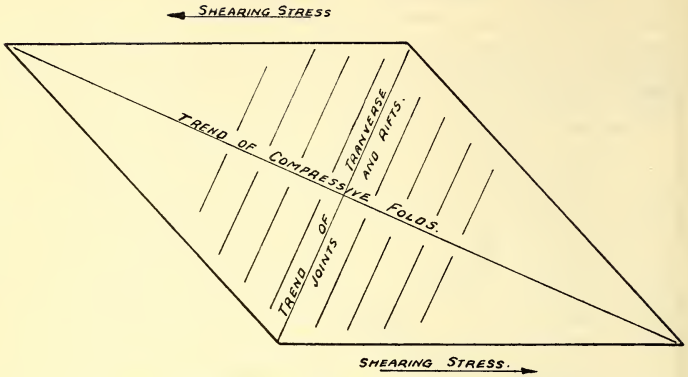


Fig. 2.—Relief of shearing stress by folding.

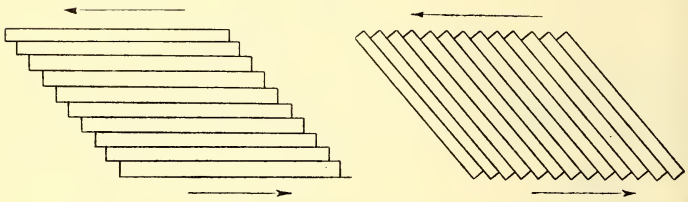


Fig. 3.—Relief of shearing stress by high angle faulting.

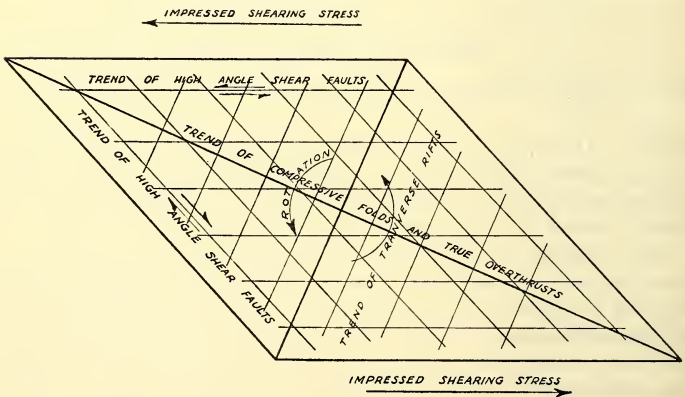


Fig. 4.—The strain rhomb—showing the strain set up in a square section by impressed shear.

tion may produce echelon domes and basins with fold axes parallel to the compressional direction. Here it is usual to find that the trace of the axial planes have curving or inflected shapes.

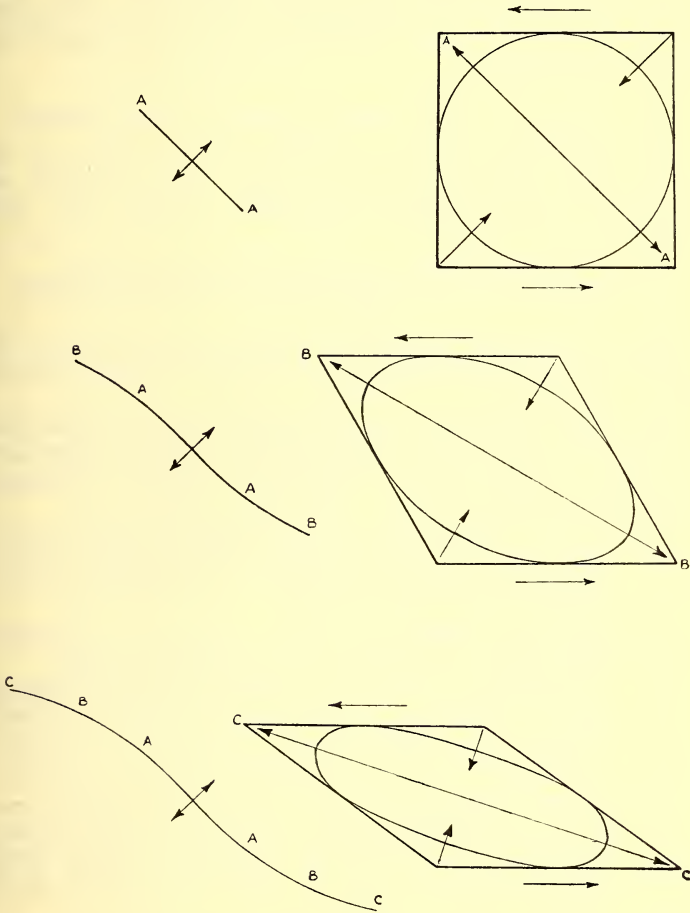


Fig. 5.—Genesis of sigmoid or inflected anticlines.

The genesis of these inflected structures is illustrated by the serial diagrams of Fig. 5. Consider the case of a circle being deformed within a square by impressed shear. The initial compression folds are in the direction AA. As

deformation proceeds, though the fold continues to develop in amplitude about the AA trend in the medial section, longitudinal increments to the fold take the trend AB, owing to the progressive rotation of the azimuth of the axis of compression. Still later extensions take the trend BC. The net result is an anti-clockwise axis which in plan looks like an elongated integration symbol—a sigmoid anticline.

APPLICATION TO THE LATE PALÆOZOIC STRUCTURES.

The following features, all of which we now believe to be genetically related, have suggested the operation of rotational and possibly torsional stresses in the Carboniferous terrain.

1. Fault Patterns in the Hunter Region and in the Werrie Basin.

Reference should be made to Osborne (1922, 1926, 1927, 1928) and especially to maps in Osborne (1929), also to Carey (1934).

The faults and folds of these districts, varied as they are in magnitude, direction, and character, may be classified, according to the present discussion, into the following groups (see Fig. 6).

- (a) *Shear Thrusts, Group A*: Hunter Thrust, Brushy Hill Fault (?), Mooki Thrusts, Goorangoola Fault, Welshman's Creek Fault.
 - (b) *Shear Thrusts, Group B*: Paterson, Glenoak, Butterwick, Charlton and Lennoxton Faults.
- The angular relations of these two groups suggest that they are conjugate shear systems, developed during rotational stress. This is a reading alternative to that of Osborne (1929, pp. 440-2).
- (c) *Faults intimately related to the compressive component of the diastrophism*: Williams River Fault, Fishhole Creek Fault, Mirannie Fault, East Westbrook Fault, Dry Creek Fault and Mt. Olive Fault.
 - (d) *High Angle Faults in the Tensional Direction*: Webber's Creek Fault, Manresa Fault, Benvenue Fault, and Owens Mount Fault.

The Webber's Creek Fault, one of the most important in the Hunter District, separates two distinct structural provinces, viz. the Cranky

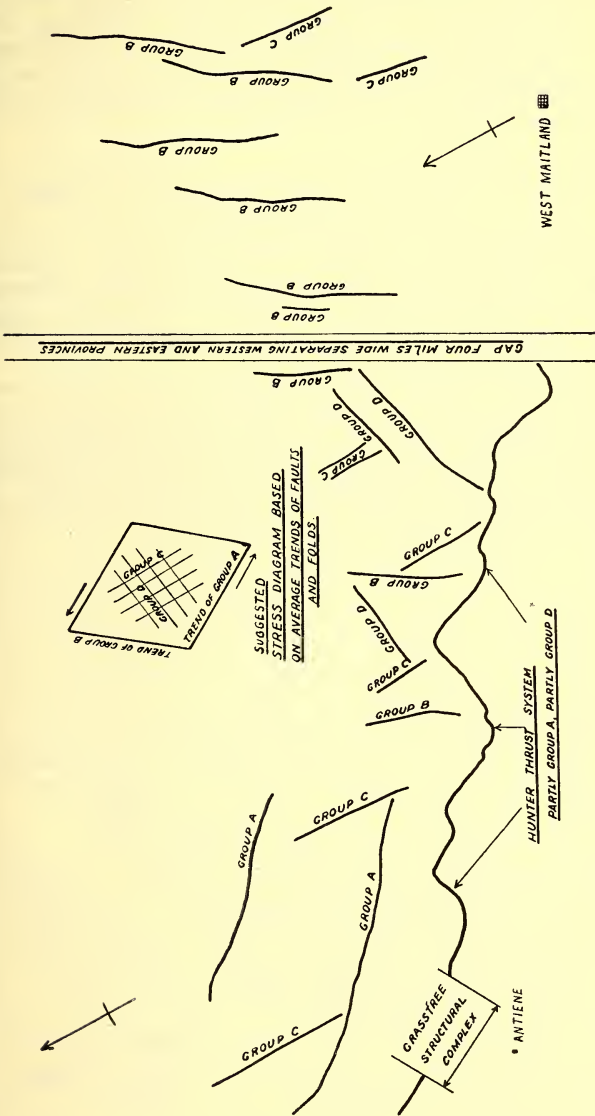


Fig. 6.—Possible interpretation of fracture-systems in Carboniferous terrain of Hunter Valley.

Corner Basin and the Mirannie Basin, and presents many outstanding features. Extending the view previously expressed (Osborne 1929, p. 443), one may now regard it partly as a high angle tensional shear running at right angles to the direction of the compressive component of the diastrophism.

II. Domes and Basins Due to Compressive Stress Accompanying Shearing.

Stroud-Gloucester Trough, Williams River Pitching Anticline, Wallarobba Dome, Lamb's Valley Pitching Anticline, Cranky Corner Basin, Mirannie Basin, Moonabung Basin and Owens Mount Basin.

Some of these folds possess curving or inflected axes. The axis of the Owens Mount Basin shows curving in a direction different from that of the other inflected folds, and we are of the opinion that the peculiar structural environment of the Grasstree region is responsible for the conditions shown on the diagram, Fig. 7.

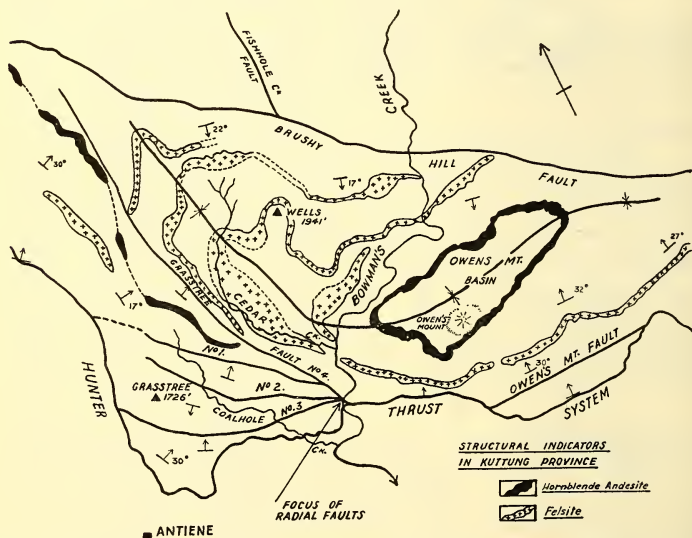


Fig. 7.—Radial faults and inflected fold-axis in complex structural environment near Owens Mount.

III. Irregularities of Strike and Dip of the Border Thrusts.

Attention has already been drawn to the fact that the thrust surfaces of the Hunter and Mooki Systems are very irregular and show abrupt changes in both strike and dip (Osborne, 1929, pp. 446-7, and Carey, 1934, p. 365). An analysis of these irregularities in the Werrie Basin showed (*loc. cit.*) that a strong shearing component is implied in the causal stresses.

In the region between Scone and Sedgefield, particularly, the relation of the Hunter Thrust lines and the directions of other faults to the east indicates that the steep tensional fractures, of which the Webber's Creek Fault is the most conspicuous, and the members of Shear Group B have combined to give the distinctive pattern of part of the border thrust-zone (see Fig. 6).

IV. Groups of Radial Faults.

In at least three places in the Middle and Lower Hunter district there are sets of cognate faults radially disposed from centres which are always located in a complex structural environment. Two such sets in the Carboniferous belt are in the neighbourhood of Grasstree Trigonometrical Station and near Gosforth. At the former locality the bundle of fractures, closely associated as they are with the strongly curved attitude of the Owens Mount Basin (with its apparently anomalous trend) is evidence suggestive of torsional stresses having operated. Further, the general arrangement of the shear patterns throughout the Hunter region is complex, and the variation in the orientation of the principal axes of shearing may again be expressive of the operation of torsional stress.

REGIONAL TECTONIC ENVIRONMENT.

Finally we consider that the most complex structural environment occurs along the southern margin of the New England Province extending through the Hunter Valley, to the lower Manning District, and it is here that we must look for the lateral accommodation between the active advance of the Hunter-Bowen orogen and the belt to the south that was little, if at all, affected by the late Palæozoic movements. The orogen, north of the Hunter region, is marked by a relatively simple relationship between the dominant folds and faults—a feature contrasting strongly with the complexities of the conflicting structural systems in the south.

FUTURE WORK.

One of us (G.D.O.) has undertaken the working out of the patterns of the structures and their interpretation as shear-systems in order to elucidate the tectonic evolution and to determine the nature of the causal stresses. Such an analysis may provide critical evidence as to whether the stresses which deformed the Upper Palæozoic rocks were exerted from the ocean towards a continental mass, or through outward sub-continental movement within the sub-stratum, or again whether the continental materials were themselves active.

ACKNOWLEDGMENT.

Indebtedness is expressed to the Trustees of the Science and Industry Endowment Fund, Commonwealth C.S.I.R., for having made available a grant to one of the authors (G.D.O.) towards the expenses of the field work on which this paper largely depends.

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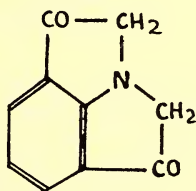
RESEARCHES ON INDOLES.*

PART VII. DERIVATIVES OF 7-NITROINDOLE.

By GORDON K. HUGHES, B.Sc.,
 FRANCIS LIONS, B.Sc., Ph.D.,
 and ERNEST RITCHIE, B.Sc.

(Manuscript received, November 23, 1938. Read, December 7, 1938.)

Jackson and Kenner (*J.C.S.*, 1928, 573) have discussed some of the more important chemical evidence for the co-planar distribution of the valencies of tervalent nitrogen, and have pointed out that since most of the conclusions in favour of a planar distribution rest on negative rather than positive evidence, additional positive evidence would be most desirable. They suggested that this evidence "might be supplied by the preparation of a compound in the molecule of which a nitrogen atom is common to two ring structures which are at the same time plane and co-planar"; and that a suitable compound might be (I). They pointed out the necessity of the two rings attached to the benzene

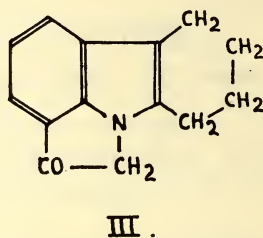
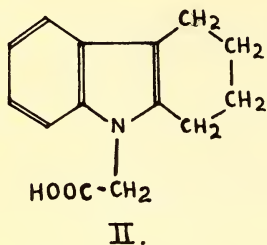


I.

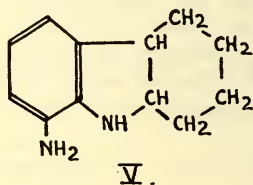
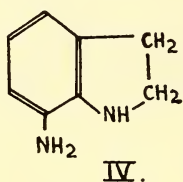
ring being five-membered for any conclusions in favour of the planar disposition of the nitrogen valencies to be valid. Jackson and Kenner's experiments were inconclusive and a compound of the type sought could not be obtained. It will be recalled that Perkin and Reilly (*J.C.S.*, 1923, 2399) had previously recorded the absence of any tendency of tetrahydrocarbazole-9-acetic acid (II)

* For Part VI of this series, see *THIS JOURNAL*, 1937-8, 71, 494.

to pass over into the corresponding anhydro derivative (III), which would have been of the type sought.



The normal behaviour of 8-aminotetrahydroquinoline as a monoalkylated *o*-phenylene diamine (cf. Hazlewood, Hughes and Lions, *Journ. Proc. Roy. Soc. N.S.W.*, 1937, 81, 462-474), and its ability to form heterocyclic substances of various types, suggested that it would be of considerable interest to prepare 7-aminodihydroindole (IV) and 8-amino-hexahydrocarbazole (V) and to study closely the possibility



of closing new five-membered heterocyclic ring systems containing both the nitrogen atoms already present in these two substances with a view to obtaining evidence on the nitrogen valency disposition. The present paper describes the results of a necessary preliminary investigation which had as its object the synthesis of derivatives of 7-nitroindole. Several nitroindoles have been prepared in the past, but since the application of the Fischer synthesis to the cyclisation of nitrophenylhydrazones is often uncertain, we have thought it of value to study the conditions best suited to the preparation of 7-nitroindoles somewhat closely.

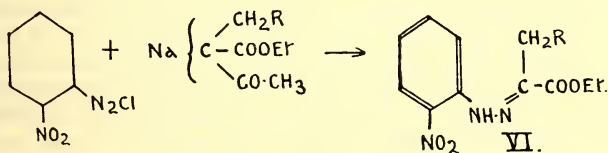
Ekenstein and Blanksma (*Rec. Trav. Chim.*, 24, 37) prepared the *o*-nitrophenylhydrazones of acetone, diethylketone and acetophenone but did not describe the cyclisation of these to 7-nitroindoles. Borsche (*Annalen*, 1908,

359, 49), however, prepared the o-, m- and p-nitrophenylhydrazones of cyclohexanone, and cyclised them to the corresponding nitrotetrahydrocarbazoles by heating with dilute sulphuric acid at 100° for 30 minutes. Again, in 1932, Bauer and Strauss showed that the o-, m- and p-nitrophenylhydrazones of methyl ethyl ketone could be cyclised to the corresponding nitrodimethyl indoles by heating with concentrated hydrochloric acid; whilst similar treatment converted the o-, m- and p-nitrophenylhydrazones of propion aldehyde to the corresponding propylidene dinitrodiskatols.

Apart from these results it should be recalled that Borsche and Rentschell (*Annalen*, 1911, 379, 178) obtained 1-hydroxy-2-methyl-4-nitroindole by reduction of 2:6-dinitrophenylacetone with amyl mercaptan; and that Majima and Kotake (*Berichte*, 1930, 63, 224) obtained 6-nitroindole by decarboxylation of 6-nitro-3-carboxyindole the ethyl ester of which was obtained by direct nitration of 3-carbethoxy indole.

We have prepared several new o-nitrophenylhydrazones from o-nitrophenylhydrazine and aldehydes and ketones and have attempted the cyclisation of these to indoles, but, except in one or two instances, without success. From our experience it appears that o-nitrophenylhydrazones derived from aldehydes or ketones with a methylene group (not methyl) adjacent to the carbonyl group are capable of cyclisation; but it should be noted that the o-nitrophenylhydrazone of desoxybenzoin could not be induced to pass over into the corresponding 7-nitro-2:3-diphenylindole.

Greater success attended the preparation of 7-nitroindole-2-carboxylic esters by cyclisation of the intermediate o-nitrophenylhydrazones of α -keto esters, which were obtained in satisfactory yields by coupling diazotised o-nitroaniline with the alkali derivatives of various monoalkylated acetoacetic esters—the Japp-Klingemann reaction (cf. *Berichte*, 1888, 21, 549; *Annalen*, 247, 218).



(R=H, -CH₃, -C₂H₅, n -C₃H₇, -C₃H₆COOH, -C₆H₅)

The discovery of conditions suitable for the cyclisation of the intermediates (VI) to the corresponding indoles has occasioned the carrying out of very numerous experiments, and, although success has been achieved in most circumstances, it is not possible to formulate a set of conditions which invariably leads to success, a method which works well with one particular nitrophenylhydrazone, being useless for the cyclisation of a second, and so on. The most generally useful reagent was found to be anhydrous zinc chloride in boiling cumene solution, but even this reagent failed in some instances, where, curiously enough, hydrobromic acid in glacial acetic acid, or even alcoholic hydrochloric acid were effective.

It is worthy of record that treatment of the yellow *o*-nitrophenylhydrazone of ethyl α -ketobutyrate (VII; m.pt. 94°) obtained from ethyl α -acetyl butyrate and diazotised *o*-nitroaniline with either glacial acetic acid or alcoholic hydrogen chloride led not to indole ring closure but to formation of an isomeric substance (VIII) melting at 68° . The isomerism of (VII) and (VIII) is probably steric, the two substances being geometrical isomers (cf. article by Meisenheimer and Theilacker in "Stereochemie", ed. Freudenberg, Leipzig, 1933). Both (VII) and (VIII) can be induced to undergo the Fischer indole ring closure by boiling with concentrated aqueous hydrochloric acid, 3-methyl-7-nitroindole-2-carboxylic acid being obtained from the reaction mixture. The rate of cyclisation varies considerably with the two isomers.

EXPERIMENTAL.

Preparation of o-Nitrophenylhydrazones of α -Keto-esters.

The details of the general method employed were as follows: An ice-cold solution of potassium hydroxide (50% ; 51 c.c.) was added to an efficiently stirred solution of the substituted acetoacetic ester (1/7th gram mol.) in absolute alcohol (150 c.c.) at 0° . Ice-water (300 c.c.) was then added, and, without delay, the diazo solution from *o*-nitroaniline (20 g. ; 1/7th gram mol.), concentrated hydrochloric acid (60 c.c.), sodium nitrite (10.5 g.) and water (90 c.c.) rapidly run in. The stirring was continued for a further 5 minutes and the separated *o*-nitrophenylhydrazone collected. If an oil, it was taken up in ether, washed with 5% sodium hydroxide solution, then water, dried, and the solvent removed. If solid it was collected and recrystallised from a suitable solvent. The oily

nitrophenylhydrazone could not be distilled even at 2 mm. pressure, owing to excessive frothing.

Methods of Cyclisation of Intermediate o-Nitrophenylhydrazones.

The following methods were all employed in attempts to effect the Fischer indole ring-closure of the intermediate o-nitrophenylhydrazones :

(1) A solution of the o-nitrophenylhydrazone (hereafter designated O.N.P.) in ten times its weight of glacial acetic acid was refluxed for several hours, then poured into water. The product was then recovered with the aid of ether and examined.

(2) The O.N.P. was dissolved in ten times its weight of cold concentrated sulphuric acid, and the solution allowed to stand for 24 hours. It was then poured on to crushed ice and the product recovered with ether as before.

(3) Dry hydrogen chloride was rapidly passed into a hot solution of the O.N.P. in absolute alcohol until ammonium chloride precipitated. Then, after standing two hours, the mixture was poured into water and the product recovered, as before, with ether.

(4) The O.N.P. was refluxed with ten times its weight of dilute sulphuric acid (1 : 10) until no further apparent change occurred. If a solid precipitate remained it was filtered off, collected by filtration, prior to purification ; if, however, the product was tarry the acid aqueous liquor was decanted and the residue washed with water, and then extracted with hot dilute sodium carbonate solution. After filtration the cooled extract was acidified and any precipitated acid recovered and purified.

(5) The same procedure was employed as described for (4), except that concentrated hydrochloric acid was employed instead of dilute sulphuric acid.

(6) This method follows that of D.R.P. 238,138 (cf. Friedländer, Vol. X, p. 332). Powdered anhydrous zinc chloride was added to a solution of the O.N.P. (1 part) in cumene (3 parts) and the whole gently refluxed for 3 hours. The solvent was then removed with steam and the residue collected with ether and examined.

(7) Anhydrous zinc chloride (20 g.) was dissolved in a solution of the O.N.P. (2 g.) in absolute alcohol (16 c.c.) and the mixture heated under reflux for two hours. It was then poured into ice-water, made faintly acid and the product collected with ether.

(8) The O.N.P. was dissolved in ten times its weight of a solution of hydrogen bromide in glacial acetic acid and the solution refluxed for 90 minutes, then poured into water. The precipitated product was collected with ether and purified.

Ethyl pyruvate o-Nitrophenylhydrazone.

This O.N.P. (30 g.) was obtained by the general method from ethyl α -acetyl pyruvate (20.5 g.) and diazotised o-nitroaniline (20 g.). It came out from alcohol in yellow needles melting at 106°.

Found: N=16.5%; calculated for $C_{11}H_{13}O_4N_3$, N=16.7%.

7-Nitroindole-2-carboxylic Acid.

Attempts to effect cyclisation of ethyl pyruvate o-nitrophenylhydrazone to an indole by methods (1), (2) and (3) all failed, but it was possible to isolate 7-nitroindole-2-carboxylic acid from the product of reaction by method (5), 5 grams of hydrazone yielding 3 grams of the acid. It came out in yellow needles from alcohol, melting at 231°.

Satisfactory analyses of this substance could not be obtained. A typical result was:

Found: N=16.5%; calculated for $C_9H_6O_4N_2$, N=13.6%.

A determination of the equivalent weight was made by the silver salt method from the bright red silver salt. This tended to decompose explosively on heating, which may account for the high value found, 216 instead of the theoretical 206.

The nitroindole carboxylic acid dissolves readily in cold dilute alkali to a yellow solution which becomes red on warming. Attempts to prepare 7-aminoindole-2-carboxylic acid with the help of ferrous sulphate and ammonia proved abortive.

7-Nitroindole.

7-Nitroindole-2-carboxylic acid (10 g.) and anhydrous glycerol (100 c.c.) were heated carefully to 220° and maintained at that temperature until all the solid had disappeared (3 to 5 minutes). The reaction mixture was then cooled and poured into water, and the nitroindole (yield 60%) collected with ether. It was finally rapidly distilled *in vacuo*, when it came over between 170° and 175° at 32 millimetres pressure, and at once solidified.

After recrystallisation from petroleum ether it was obtained in orange platelets melting at 113° .

Found : C=57.2, H=5.3% ; calculated for $C_8H_6O_2N_2$, C=59.3, H=3.7%.

Ethyl α -Ketobutyrate o-Nitrophenylhydrazone (A).

Obtained in 90% yield by the general method from ethyl α -acetyl butyrate and diazotised o-nitraniline, this O.N.P. was recrystallised from alcohol, and thus obtained in yellow needles melting at 94° .

Found : N=15.5% ; calculated for $C_{12}H_{15}O_4N_3$, N=15.4%.

Attempts to cyclise this substance by methods (1) or (3) converted it into an isomeric yellow crystalline isomer (B) melting at 68° .

Found : N=15.4% ; calculated for $C_{12}H_{15}O_4N_3$, N=15.4%.

That this substance was probably a geometrical isomer is shown by the fact that it could be converted into the 3-methyl-7-nitro-indole-2-carboxylic acid described below by boiling with concentrated hydrochloric acid ; but it is worthy of comment that the ease of cyclisation was considerably less than for the isomeric (A).

Ethyl-3-Methyl-7-Nitroindole-2-Carboxylate.

Cyclisation of the ethyl α -ketobutyrate o-nitrophenylhydrazone (A) described above, by the method (2) readily yielded the corresponding indole ester, ethyl 3-methyl-7-nitroindole-2-carboxylate, which was obtained in small yellow nacreous plates, melting at 115° , from methyl alcohol.

Found : N=11.1% ; calculated for $C_{12}H_{12}O_4N_2$, N=11.3%.

3-Methyl-7-Nitroindole-2-Carboxylic Acid.

Cyclisation of either of the isomeric ethyl α -ketobutyrate o-nitrophenylhydrazones (A or B) by method (5) yields 3-methyl-7-nitroindole-2-carboxylic acid, which can be obtained in yellow needles melting above 270° from alcohol. The acid may also be obtained by hydrolysis of its ethyl ester obtained as described above.

Found : N=12.8% ; calculated for $C_{10}H_8O_4N_2$, N=12.7%.

Ethyl α -Ketovalerate o-Nitrophenylhydrazone.

On coupling o-nitraniline (15 g.) and ethyl α -acetylvalerate (18 g.) by the general method, this O.N.P. was obtained as a dark red oil (28 g.) which could not be induced to crystallise. Attempts to purify it by distillation at 2 mm. failed because of excessive frothing. Although this substance was not analysed, its cyclisation to the products described below leaves no doubt that the constitution ascribed to it is correct.

Ethyl-3-Ethyl-7-Nitroindole-2-Carboxylate.

Although method (1) failed to effect cyclisation of ethyl α -ketovalerate o-nitrophenylhydrazone to an indole; the application of either methods (2) or (6) yielded the corresponding indole ester without difficulty. After recrystallising from methyl alcohol, ethyl 3-ethyl-7-nitroindole-2-carboxylate formed yellow needles melting at 85°.

Found: N=10.9%; calculated for $C_{13}H_{14}N_2O_4$, N=10.7%.

3-Ethyl-7-Nitroindole-2-carboxylic Acid.

On treating ethyl α -ketovalerate o-nitrophenylhydrazone with boiling concentrated hydrochloric acid (method (5)) a tar was formed, from which hot dilute sodium carbonate extracted 3-ethyl-7-nitroindole-2-carboxylic acid. It crystallised from methyl alcohol as yellow prisms, which melted with evolution of carbon dioxide at 245°.

Found: N=11.9%; calculated for $C_{11}H_{10}O_4N_2$, N=12.0%.

Ethyl α -Ketocaproate o-Nitrophenylhydrazone.

Diazotised o-nitraniline (10 g.) was coupled with the potassium salt of ethyl α -acetyl caproate by the general procedure. The O.N.P. formed a dark red oil (15 g.), which like its next lower homologue could not be distilled, or induced to crystallise. Its constitution follows, however, from the nature of its cyclisation products.

Ethyl-3-Propyl-7-Nitroindole-2-Carboxylate.

The application of method (1) fails to effect cyclisation of ethyl α -ketocaproate o-nitrophenylhydrazone to the corresponding indole ester, but both methods (2) and (6) yield ethyl-3-propyl-7-nitroindole-2-carboxylate smoothly.

This indole ester after recrystallisation twice from methyl alcohol formed yellow needles which melted at 70°.

Found: N=10.0%; calculated for $C_{14}H_{16}O_4N_2$, N=10.1%.

3-Propyl-7-Nitroindole-2-Carboxylic Acid.

Treatment of the O.N.P. by method (5) yields a dark tar from which 3-propyl-7-nitroindole-2-carboxylic acid may be isolated by extraction with hot dilute sodium carbonate, followed by acidification.

After recrystallising from methyl alcohol and benzene the indole acid forms pale yellow needles which melt at 196°.

Found: N=11.5%; calculated for $C_{12}H_{12}O_4N_2$, N=11.3%.

Ethyl Phenylpyruvate o-Nitrophenylhydrazone.

Ethyl α -acetylphenylpropionate (32 g.) and diazotised o-nitraniline (20 g.) reacted as in the general method, gave the O.N.P. as a dark red oil (41 g.). A solution of this oil in light petroleum, however, deposited the O.N.P. as orange prisms when it was allowed to evaporate slowly at room temperature. The crystals thus obtained melted at 68°.

Found: N=12.2%; calculated for $C_{17}H_{17}O_4N_3$, N=12.8%.

Ethyl-3-Phenyl-7-Nitroindole-2-Carboxylate.

The cyclisation of ethyl phenyl pyruvate o-nitrophenylhydrazone to an indole afforded some difficulty. Methods (1), (2), (4), (5) and (6) were of no avail, but methods (3) and (8) cyclised the O.N.P. to the corresponding indole ester. Method (3) gave a yield of 60%, but this product was much more difficult to purify than that obtained by method (8), in which a yield of 45% was obtained. After recrystallising from benzene and methyl alcohol, ethyl-3-phenyl-7-nitroindole-2-carboxylate forms yellow prisms which melt at 112°.

Found: N=9.0%; calculated for $C_{17}H_{14}O_4N_2$, N=9.0%.

o-Nitrophenylhydrazone of the Half-ester of α -Ketopimelic Acid.

Diazotised o-nitraniline (10 g.) was reacted with the potassium salt of ethyl cyclohexanone-2-carboxylate (12 g.)

by the general method and the product collected from the weakly acidified solution. Recrystallised from methyl alcohol it formed small yellow prisms melting at 122°.

Found: N=12.6%; calculated for $C_{15}H_{19}O_6N_3$, N=12.5%.

Attempts to cyclise this substance to an indole by method (2) all failed. By method (6) water was apparently split off, but a tar was formed. From the product obtained by application of method (5) it was possible to extract an acidic substance with sodium carbonate solution, and this after recrystallisation once from methanol and twice from benzene formed pale yellow prisms melting at 171°.

Found: N=9.0%; calculated for $C_{13}H_{12}O_6N_2$, N=9.5%.

This product was thus, apparently, γ (-2-carboxy-7-nitroindolyl)-butyric acid.

By application of method (7) to the intermediate O.N.P. it was possible to obtain in small yield (5-10%) a pale yellow material which crystallised in plates melting at 184° from methyl alcohol.

Found: N=8.6%; calculated for $C_{15}H_{16}O_6N_2$, N=8.7%.

This substance is thus the expected γ -(2-carbethoxy-7-nitroindolyl)-butyric acid.

Preparation of o-Nitrophenylhydrazones of Aldehydes and Ketones, and Cyclisation Experiments with these.

A warm aqueous solution of o-nitrophenylhydrazine hydrochloride (6 g. in 80 c.c.) was treated with a solution of the theoretical amount of the aldehyde or ketone in a little alcohol. After standing for 30 minutes much water was added to the reaction mixture and the completely precipitated O.N.P. filtered off and then recrystallised from a suitable solvent. The yields were usually very good.

Attempts to effect indole ring closure were then made, using the methods outlined above. The results obtained are recorded under the individual O.N.P.'s.

Acetone o-Nitrophenylhydrazone.

In agreement with Ekenstein and Blanksma (*Rec. Trav. Chim.*, 1905, 24, 37) this O.N.P. melted at 70°. It could not be cyclised using methods (5) or (6).

Diethylketone o-Nitrophenylhydrazone.

In agreement with Ekenstein and Blanksma (*loc. cit.*) this O.N.P. melted at 60°. An attempt to effect indole

cyclisation by method (1) failed, but with method (5) *2-ethyl-3-methyl-7-nitroindole* was obtained, and after recrystallisation from petroleum ether it formed orange plates melting at 104° .

Found: N=13.5%; calculated for $C_{11}H_{12}O_2N_2$, N=13.7%.

Isobutyraldehyde o-Nitrophenylhydrazone.

This O.N.P. was obtained in small orange needles, m.pt. 59° , after recrystallisation from alcohol.

Found: N=20.4%; calculated for $C_{10}H_{13}N_3O_2$, N=20.3%.

When treated by method (5) a product was obtained which, after recrystallisation from petroleum ether, formed small orange leaflets melting at 154° . It was insoluble in concentrated hydrochloric acid.

Found: N=13.2%; calculated for $C_{24}H_{26}O_4N_4$, N=13.0%.

This substance may thus be 2:2'-isobutylidene-bis-(3:3'-dimethyl-7-nitroindolenine). Similar products have been described by Bauer and Strauss (*loc. cit.*).

Treatment of the O.N.P. by method (7) apparently caused indole cyclisation, but the product was contaminated with much tar and could not be purified.

Cyclopentanone o-Nitrophenylhydrazone.

Recrystallised from ethyl alcohol this was obtained in long orange needles melting at 64° .

Found: N=18.7%; calculated for $C_{11}H_{13}O_2N_3$, N=19.1%.

Although Perkin and Plant (*J.C.S.*, 1923, 123, 3245) were able to cyclise cyclopentanone phenylhydrazone to dihydrocyclopentindole with hot dilute sulphuric acid, attempts to prepare an indole from the O.N.P. by methods (2), (4) or (5) were all abortive.

Acetophenone o-Nitrophenylhydrazone.

In agreement with Ekenstein and Blanksma this product melted at 138° . Attempts to effect cyclisation to an indole by methods (2), (5) and (6) all failed.

Propiophenone o-Nitrophenylhydrazone.

After recrystallisation from alcohol this substance formed scarlet needles melting at 120° .

Found: N=14.9%; calculated for $C_{15}H_{15}O_2N_3$, N=15.6%.

No cyclisation could be effected by method (5), but by method (6) a mixture of red and orange crystals melting at about 70° was obtained. Even with a heating period of 6 hours in method (6) a complete conversion could not be effected.

Desoxybenzoin o-Nitrophenylhydrazone.

This O.N.P. was obtained in scarlet leaflets, m.pt. 125°, from ethyl alcohol.

Found: N=12.4%; calculated for $C_{20}H_{17}O_2N_3$, N=12.7%.

Attempts at cyclisation of this O.N.P. by methods (5) and (6) both failed.

β-Acetylpyridine o-Nitrophenylhydrazone.

This O.N.P. was obtained in felted orange needles, m.pt. 144°, from alcohol.

Found: N=21.1%; calculated for $C_{13}H_{12}O_2N_4$, N=21.5%.

No success attended efforts to obtain an indole from this substance by either methods (5) or (6).

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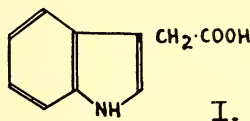
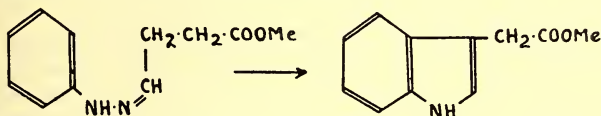
RESEARCHES ON INDOLES.

PART VIII.—3-HYDROXYMETHYL INDOLE-2-CARBOXYLIC ACID LACTONE.

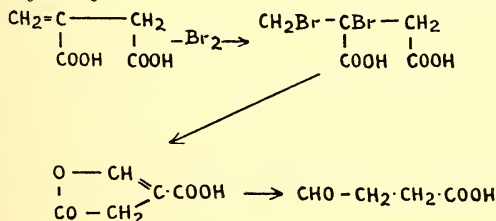
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and FRANCIS LIONS, B.Sc., Ph.D.

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The demonstration by Kögl, Haagen-Smit and Erxleben (*Z. physiol. Chem.*, 1934, 228, 90-103) that heteroauxin is identical with indole-3-acetic acid (I) has focussed attention on the methods available for its synthesis. Unfortunately, it is not a very readily accessible substance, although several methods for its preparation appear in the literature. The first recorded synthesis is that of Ellinger (*Berichte*, 1904, 37, 1806), who cyclised with acid the phenylhydrazone of methyl β -aldehydopropionate.



The methyl β -aldehydopropionate was obtained by esterification of the corresponding β -aldehydopropionic acid (II) through its silver salt. This acid in turn was prepared either by conversion of itaconic acid to aconic acid and hydrolysis of the latter with water as shown :

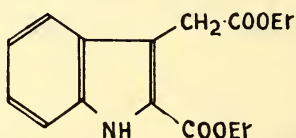


or by the method of Perkin and Sprankling (*J.C.S.*, 1899, 75, 11), in which bromoacetal is condensed with ethyl sodio malonate, the resulting ester hydrolysed to acetalmalonic acid and the latter converted to β -aldehydopropionic acid (II) by prolonged hydrolysis with water at 180-190°. Another method of preparation of β -aldehydopropionic acid was described recently by Jackson and Manske (*Canadian Journal of Research*, 1935, 13, 170), who prepared β -cyanopropionacetal and effected its hydrolysis in two stages to (II).

Aldehydopropionic acid itself may be treated with phenylhydrazine, when the phenylhydrazone of β -aldehydopropionic phenylhydrazide is obtained, and this reacts with ethyl alcoholic sulphuric acid to form ethyl indole-3-acetate.

The next described method of synthesis of (I) is due to Majima and Hoshino (*Berichte*, 1925, 58, 2042) and depends upon the fact that the cyano group is indifferent to indolyl-magnesium iodide. When this is treated with chloroacetonitrile in presence of cold anisole or ether, an additive product is obtained, which when heated to 60-70°, then decomposed by water yields β -indolylacetonitrile. This is readily hydrolysed with alkali to indole-3-acetic acid. It is not possible to replace the chloroacetonitrile used in this synthesis by the more readily accessible bromo- or chloroacetic ester, as it has been shown by Wegler and Binder (*Arch. Pharm.*, 1937, 506) that indolyl magnesium iodide reacts with the ester grouping in preference to the halogen.

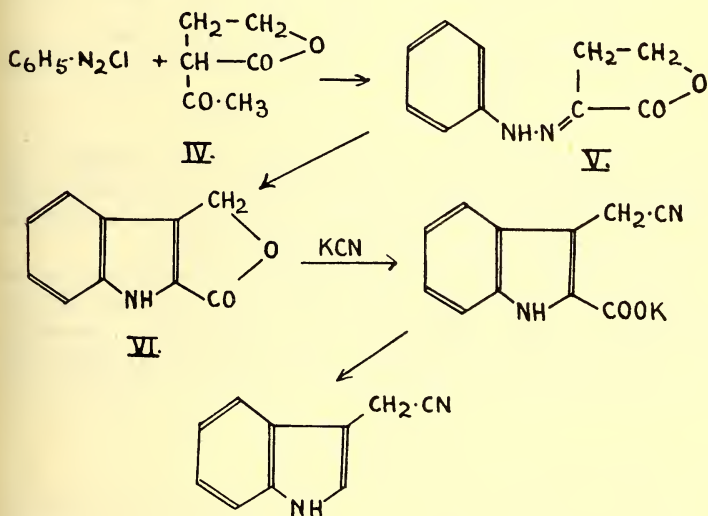
In 1934 King and L'Ecuyer (*J.C.S.*, 1934, 1901) endeavoured to prepare (I) in satisfactory yield by cyclisation of the phenylhydrazone of the half ester of α -keto-glutaric acid (obtained by the Japp-Klingemann reaction from benzene diazonium chloride and ethyl α -acetylglutarate) to ethyl 2-carbethoxy indole-3-acetate (III), with alcoholic hydrochloric acid, followed by hydrolysis and selective decarboxylation of the acid corresponding to (III). They were able to obtain (I) but only in very small yield.



III.

The most satisfactory recorded synthesis of (I) is due to Jackson and Manske (*loc. cit.*), who reacted ethyl diazoacetate with indole and thus obtained indole-3-acetic ester, some 1:3-indolylene diacetic ester being also obtained as a by-product.

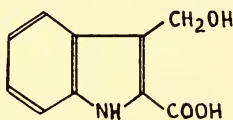
Of the methods of synthesis of (I) so far described those of Majima and Hoshino and of Jackson and Manske are definitely superior to the others, but each starts from the relatively expensive indole, and the preparation of large quantities of (I) by either method would be tedious. Since the authors had accumulated a supply of acetobutyrolactone (IV) (*cf.* Knunjanz, Celincev and Osetrova, *C.R. de l'U.S.S.R.*, 1934, *I*, 315) in connection with another investigation, it appeared to be of interest to endeavour to obtain (I) by the series of reactions outlined diagrammatically below :



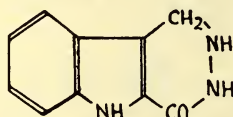
Addition of benzene diazonium chloride solution to a solution of acetobutyrolactone (IV) in sodium hydroxide solution readily yielded the phenylhydrazone of α -ketobutyrolactone (V), the acetyl group being extruded. Many attempts to effect cyclization of (V) to (VI) with various acid reagents proved abortive, but eventually it was found that gradual addition of concentrated hydrochloric acid to a boiling glacial acetic acid solution of (V)

(a method employed by Kent (*J.C.S.*, 1935, 976)) led to production in poor yield of 3-hydroxymethylindole-2-carboxylic acid lactone (VI).

The lactone nature of (VI) was shown by its insolubility in cold alkali and gradual solution in hot sodium hydroxide solution, and by the fact that acidification of a solution so prepared and then cooled led to precipitation of 3-hydroxymethyl-indole-2-carboxylic acid (VII). It was found that (VI) also reacted readily with hydrazine hydrate and with phenyl hydrazine, giving a beautifully crystalline hydrazide and phenylhydrazide respectively of (VIII). The hydrazide could be condensed with benzaldehyde, and on heating was found to lose water and so to form the cyclic hydrazide (VIII). This observation contrasts with the results of



VII.



VIII.

Wiedel (*Berichte*, 1900, 33, 768) that the hydrazide of *o*-hydroxymethylbenzoic acid, obtained by the action of hydrazine hydrate on phthalide, could not be converted to the cyclic hydrazide by dehydrating agents.

Attempts to react (VI) with potassium cyanide so as to obtain a product similar to the *o*-carboxybenzyl cyanide so obtainable from phthalide (cf. Wislicenus, *Annalen*, 233, 102) all proved abortive. The method envisaged for the preparation of (I) could, therefore, not be carried out.

EXPERIMENTAL.

Phenylhydrazone of α -Ketobutyrolactone.

To an ice-cold solution of acetobutyrolactone (20 g.) in 2.5% sodium hydroxide solution (625 c.c.) was added with vigorous stirring a diazonium solution prepared from aniline (16 g.), concentrated hydrochloric acid (45 c.c.), water (110 c.c.) and sodium nitrite (12 g.), followed by addition of sodium acetate (16 g.). The phenylhydrazone precipitated immediately as a brick red solid, which was collected after a further five minutes, washed and dried (27 g.). Recrystallised from methanol, ethanol, or glacial acetic acid, it formed very pale, apricot-coloured, lustrous

plates which gradually darkened on exposure to air. Repeated recrystallisation from dry ethyl acetate with the aid of charcoal gave colourless needles melting at 220° .

Found: N=14.8%; calculated for $C_{10}H_{10}O_2N_2$, N=14.7%.

In further experiments it was found that addition of benzene diazonium chloride to a solution of acetobutyrolactone in aqueous alkali that had previously stood at room temperature for 20 hours led to formation of the same phenylhydrazone—indicating the stability of the lactone ring.

Lactone of 3-Hydroxymethylindole-2-Carboxylic Acid.

The crude dry phenylhydrazone of α -ketobutyrolactone was used for cyclisation experiments. Attempts to effect indole ring closure with (a) saturated alcoholic hydrogen chloride, (b) alcoholic sulphuric acid, (c) concentrated hydrochloric acid, (d) concentrated sulphuric acid, (e) glacial acetic acid, and (f) hydrobromic acid in glacial acetic acid, led to formation of dark coloured amorphous products. With the first mentioned reagent ammonium chloride was observed to separate, but the product obtained by pouring the reaction mixture into water was brown, amorphous, and high melting. Somewhat more success attended the use of hydrochloric acid in acetic acid. By careful and gradual addition of concentrated hydrochloric acid (8 c.c.) to a hot solution of the phenylhydrazone (10 g.) in glacial acetic acid (60 c.c.), followed by boiling for two minutes after the ebullition due to the addition of the hydrochloric acid had subsided, and then allowing to cool, small colourless crystals of ammonium chloride separated. The supernatant black liquid was poured into water, and the brown solid which separated was collected and repeatedly extracted with boiling water. From the combined aqueous extracts yellow needles (3 g.) separated.

They were recrystallised from water containing a little alcohol or from ethyl acetate (charcoal) and thus obtained in colourless needles melting at 208° .

Found: N=8.3%; calculated for $C_{10}H_7O_2N$, N=8.1%.

This substance was insoluble in sodium carbonate solution even on boiling, and in cold sodium hydroxide solution, but it dissolved in boiling caustic alkali solution, thus indicating the retention of the lactone ring.

3-Hydroxymethylindole-2-Carboxylic Acid.

After solution of the above described indole lactone in hot dilute sodium hydroxide solution, the solution was cooled and acidified. The acid which was precipitated was collected and recrystallised several times from aqueous alcohol, and was thus obtained as an almost colourless microcrystalline powder which becomes pink and finally purple on exposure to the air. It melts at 244-245° with evolution of carbon dioxide.

Found : N=7.5% ; calculated for $C_{10}H_9O_3N$, N=7.5%.

The acidic nature of this substance is shown by its ready solubility in sodium carbonate solution.

3-Hydroxymethylindole-2-Carboxylic Acid Hydrazide.

The indole lactone (0.5 g.) was added to a boiling solution of 50% hydrazine hydrate solution (3 g.) in water (10 c.c.), and boiling continued until solution was complete. Pale yellow crystals separated from this solution on cooling. When recrystallised from water or ethyl acetate this solid came out again in colourless needles which melted at 195-200° with vigorous gas evolution when rapidly heated. If the heating were slow a change occurred at 180-200°, but the substance did not melt until 285°, cyclisation to the cyclic hydrazide (VIII) occurring.

Found : N=20.0% ; calculated for $C_{10}H_{11}O_2N_3$, N=19.4%.

The hydrazide (0.2 g.) was carefully heated (oil bath) to 180° and the temperature then gradually raised to 200° during 20 minutes. The solid did not apparently change its crystalline form, but the colour changed to yellow. The product melted at 285° but could not be recrystallised as it was insoluble in organic solvents.

Found : N=22.5% ; calculated for $C_{10}H_9ON_3$, N=22.4%.

3-Hydroxymethylindole-2-Carboxylic Acid Benzalhydrazide.

Warming of an alcoholic solution of the indole carboxylic acid hydrazide and benzaldehyde led to precipitation of the benzyldene compound in colourless plates. After recrystallisation from alcohol these commenced to melt and decompose at 235°.

Found : N=14.1% ; calculated for $C_{17}H_{15}O_2N_3$, N=14.3%.

3-Hydroxymethylindole-2-Carboxylic Acid Phenylhydrazide.

The indole lactone (0.5 g.) was heated with excess phenylhydrazine at 100° for an hour. The crystals which separated on cooling were collected and recrystallised from ethyl acetate, being thus obtained in fine needles melting at 196°.

Found: N=14.6%; calculated for $C_{16}H_{15}O_2N_3$, N=14.9%.

Fusion of the Indole Lactone with Potassium Cyanide.

A typical experiment was as follows: Finely ground potassium cyanide (6 g.) and lactone (6 g.) were intimately mixed and heated to 175-185°. The mixture frothed and darkened but did not fuse. After cooling the mass was leached out with water and the filtered solution acidified. The brown powder obtained dissolved readily in alcohol and ethyl acetate but was insoluble in water and benzene. The product was acidic, being soluble in sodium carbonate solution, and precipitated by hydrochloric acid, but it could not be crystallised or purified.

ACKNOWLEDGMENTS.

The authors gratefully express their thanks to Miss D. M. Little, B.Sc., for some of the (micro) analyses recorded in this paper. One of them (R.H.H.) also gratefully acknowledges the receipt of a Commonwealth Government Research Scholarship, which has enabled her to take part in the work.

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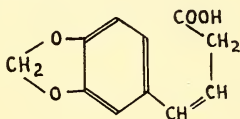
THE CONDENSATION OF PIPERONAL WITH SOME SUCCINIC ACID DERIVATIVES.

By JOHN W. CORNFORTH, B.Sc.,
GORDON K. HUGHES, B.Sc.,
and FRANCIS LIONS, B.Sc., Ph.D.

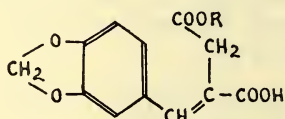
(Manuscript received, November 23, 1938. Read, December 7, 1938.)

Borsche and Eberlein (*B.*, 1914, 47, 1466) have shown that when piperonal is heated with sodium succinate and acetic anhydride at 115° for ten hours, 3:4-methylenedioxyphenylisocrotonic acid (I) is formed in poor yield. Their attempts to effect cyclisation of this substance to 6:7-methylenedioxy-1-naphthol failed owing to complete decomposition on pyrolysis.

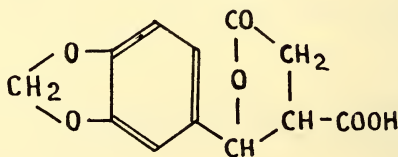
We have repeated the work of Borsche and Eberlein, and have also prepared *piperonylidenesuccinic acid* (II, R=H) and its *monoethyl ester* (II, R=C₂H₅) in order to ascertain whether these compounds could be cyclised by any method to naphthalene derivatives.



I.



II.



III.

Heating piperonal with sodium succinate and acetic anhydride for a somewhat shorter time than that previously recommended yields not only the acid (I) of Borsche and

Eberlein, but also the intermediate 3 : 4-methylenedioxyphenylparaconic acid (III). These two acids are readily separated, the former being soluble in carbon disulphide, while the latter is not. The paraconic acid (III) crystallises in plates, m.p. 164-165°, and is decomposed by heating above its melting point, carbon dioxide being evolved and the isocrotonic acid (I) formed in quantitative yield.

Attempts were made under varying conditions to effect cyclisation of the acid (I), but in all cases the only product other than unchanged material was a black tar from which no pure substance could be isolated. The acid is not affected by boiling with acetic anhydride, and attempts at cyclisation with phosphorus oxychloride led to dark uninviting products.

Piperonylidenesuccinic Acid (II, R=H) was prepared in good yield by the condensation of piperonal with ethyl succinate and sodium ethoxide, and in poorer yield by condensing piperonal with bromosuccinic ester and zinc, followed by hydrolysis of this condensation product with strong alkali. The acid crystallises in plates, m.p. 194-195°, and is readily transformed on heating with sulphuric acid in alcohol to its *monoethyl ester* (II, R=C₂H₅). On dropping this ester into "calol" previously heated to 290°, it was found that a smooth decomposition took place, and the acid (II, R=H) was regenerated, ethylene being extruded. Neither cyclisation nor disproportionation was found to occur.

Heating piperonylidenesuccinic acid with 70% sulphuric acid also failed to effect cyclisation, the only identifiable product being the unchanged acid; this was accompanied by much tarry matter.

These results indicate that $\beta\gamma$ -unsaturated acids such as (I) and (II, R=H) cannot be cyclised to naphthols without far-reaching decomposition (probably of the methylene ether ring) occurring at the same time.

EXPERIMENTAL.

Condensation of Piperonal with Sodium Succinate and Acetic Anhydride.

Piperonal (1 mol.) was heated with sodium succinate (1 mol.) and acetic anhydride (1.1 mol.) at 125° for three hours. The melt was poured into hot water, neutralised with sodium carbonate, passed through a wet filter, and extracted with ether. The ether was expelled from the aqueous phase and hydrochloric acid added. After a short

time the crude acid precipitate was collected and dried. The amount obtained did not in general exceed 20% of the amount of piperonal taken. An appreciable quantity of unchanged piperonal was always found in the ether extracts.

Separation of the two acid products was effected by extracting the mixture three times with boiling carbon disulphide. The insoluble residue was crystallised repeatedly from dilute alcohol, and finally formed plates, m.p. 164-165°, consisting of 3:4-methylenedioxyphenylparaconic acid.

Found: C=57.5, H=4.2%; equivalent weight (at 100°), 125; calculated for $C_{12}H_{10}O_6$, C=57.6, H=4.0%; equivalent weight (for a dibasic acid), 125.

The solid obtained from the combined carbon disulphide extracts, on recrystallisation from dilute alcohol, gave the acid (I) of Borsche and Eberlein, m.p. 117-118°. The amount of paraconic acid obtained was in general somewhat greater than that of the isocrotonic acid.

Pyrolysis of 3:4-methylenedioxyphenylparaconic Acid.

The acid was heated at 170° for half an hour. Decarboxylation began just above the melting point, and was soon complete. The product was cooled and dissolved in ammonia, boiled with a little animal charcoal to remove a trace of neutral slime, filtered and acidified. The acid (after recrystallisation from dilute alcohol) melted at 117-118° and was identical with that obtained as described above.

Attempted Cyclisation of Methylenedioxyphenylisocrotonic Acid.

The following methods were tried:

(i) Pyrolysis by heating at 260° for one hour. Result: dark and intractable pitch.

(ii) Pyrolysis by distillation under somewhat diminished pressure from a bath held at 260°. A distillate having a safrole-like odour but consisting almost entirely of unchanged material was obtained, and a residue of black pitch remained.

(iii) After prolonged boiling with acetic anhydride only the unchanged substance could be recovered.

(iv) Warming on water-bath with phosphorus oxychloride led to a dark tarry product from which nothing could be isolated.

3 : 4-Methylenedioxyphenylitaconic Acid (II, R=H).

(a) A mixture of piperonal (18 g.) and ethyl succinate (21 g.) was added slowly to a warm solution of sodium (7 g.) in alcohol (140 c.c.). The reaction mixture was heated on the water-bath for two hours and the alcohol then removed, water being added from time to time to replace it. The solution was now acidified with hydrochloric acid until the first traces of a precipitate appeared, and the whole then shaken out with ether. The ether was expelled from the aqueous layer and hydrochloric acid added. The precipitate was collected and dried. After two recrystallisations from glacial acetic acid 3 : 4-methylenedioxyphenylitaconic acid (piperonylidenesuccinic acid) was obtained in well formed plates which melted at 194-195°. The yield of crude product was 90% of the theoretical.

Found : C=57.4, H=4.3% ; equivalent weight, 127 ; calculated for $C_{12}H_{10}O_6$, C=57.6, H=4.0% ; equivalent weight (for a dibasic acid), 125.

(b) Zinc turnings (3.3 g.) were added to a solution of piperonal (5 g.) and diethyl bromosuccinate (12 g.) in dry benzene (60 c.c.), and the mixture heated under reflux for a considerable time (18 hours). The zinc slowly dissolved. When the reaction appeared to have ended the liquid was decanted from a slight excess of zinc and shaken out with dilute sulphuric acid. The upper layer was separated, the benzene removed, and the product saponified by heating for a short time with strong alcoholic sodium hydroxide. The alkaline liquid was extracted with ether after removal of alcohol, the ether removed from the aqueous layer, and the product (4 g.) thrown down with hydrochloric acid. After two recrystallisations from dilute alcohol the acid melted at 194-195° and was identical with the product obtained by method (a).

Ethyl Hydrogen Piperonylidene Succinate.

The acid (5 g.) was refluxed with ten times its weight of 3% alcoholic sulphuric acid for two hours. The product was poured into water, when an oil separated and rapidly crystallised. After standing in the ice-box overnight the solid was collected and recrystallised once from dilute alcohol and then once from benzene. From dilute alcohol it separated in long needles, but from benzene in rhombic plates. Both varieties of crystals melted at 130-131°.

Found : C=60.3, H=5.1% ; calculated for $C_{14}H_{14}O_6$, C=60.4, H=5.0%.

Pyrolysis of this ester was effected by dropping it into "calol" heated at 290°. A brisk evolution of gas took place. The mixture was cooled and the "calol" poured away. The residual product was washed with petroleum ether and treated with cold alkali, in which it completely dissolved. The alkaline solution was shaken out with ether, which however removed nothing. It was then acidified, and extracted with a mixture of alcohol and ether. On removal of the solvent the residue crystallised at once, and was found to consist of pure piperonylidenesuccinic acid, m.p. 194-195°.

ACKNOWLEDGMENT.

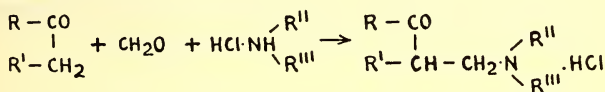
One of the authors (J.W.C.) gratefully acknowledges the receipt of a Science Research Scholarship, which has enabled him to take part in this work.

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THE USE OF MORPHOLINE FOR THE PRODUCTION OF "MANNICH" BASES.

By RITA H. HARRADENCE, M.Sc.,
and FRANCIS LIONS, B.Sc., Ph.D.*(Manuscript received, November 23, 1938. Read, December 7, 1938.)*

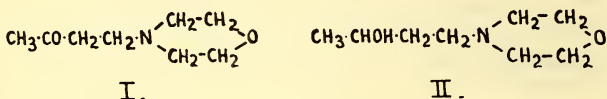
Mannich and his co-workers, in a long series of researches (published mainly in the *Archiv. der Pharmazie* and the *Berichte der deutschen chemischen Gesellschaft* during the last two decades) have closely studied the reactions between ketones containing a reactive methylene group, formaldehyde and ammonium chloride, primary aliphatic amine hydrochlorides or secondary aliphatic amine hydrochlorides. Much careful work has shown that, whereas ammonium chloride and primary aliphatic amine hydrochlorides usually give rise to several different reaction products, secondary aliphatic amine hydrochlorides, on the other hand, usually react with formaldehyde and reactive keto-methylene compounds in a straightforward way, and that the reactions can be expressed by the general equation



The resultant ketonic tertiary base hydrochlorides are readily obtainable in excellent yields, and usually afford the bases themselves in the pure condition without difficulty, although rigid purification of these is sometimes not easy. The general chemical character of these "Mannich" bases has been fairly completely elucidated, and their great usefulness as synthetic reagents for certain purposes is now well established. The present paper describes the use of the saturated heterocyclic base morpholine in the preparation of "Mannich" ketonic tertiary bases. Morpholine has recently become one of the cheapest and most accessible tertiary bases, and has the power of conferring high crystallising power on its

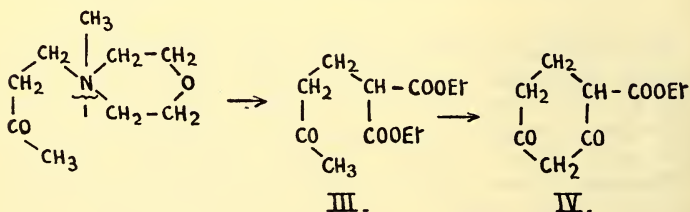
derivatives (cf. Harradence and Lions, *Journ. Proc. Roy. Soc. N.S.W.*, 1936, 70, 406-412).

When acetone is reacted in alcoholic solution with morpholine hydrochloride and paraformaldehyde it readily forms the crystalline 1-morpholinobutan-3-one hydrochloride, and from this salt the base (I) is easily obtained as a colourless oil with alkali.



It can be distilled *in vacuo*, but some decomposition occurs during the distillation. When (I) is reduced with aluminium amalgam and moist ether it affords 1-morpholinobutan-3-ol (II), an oily amino alcohol. Because the esters of amino alcohols are frequently local anæsthetics, it was deemed of value to prepare the benzoate and also the p-nitrobenzoate of (II).

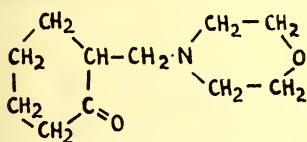
The observation of du Feu, McQuillin, and Robinson (*J.C.S.*, 1937, 53) that the quaternary halides derived from Mannich bases with alkyl halides will react readily with the sodio derivatives of such substances as β -ketonic esters, suggested that a useful method for the synthesis of dihydroresorcylic ester (IV) would consist in the condensation of the methiodide of (I) with sodio diethyl malonate in presence of sodium ethoxide, according to the scheme:



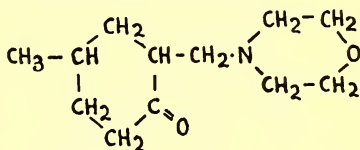
The methiodide of (I) condensed readily with sodio malonic ester to ethyl α -carbethoxy- δ -keto caproate, but the further cyclisation to (IV) was not observed to occur. III was characterised by formation of a semicarbazone and dinitrophenylhydrazone, and by its hydrolysis to the

γ -acetylbutyric acid previously prepared by Bentley and Perkin (*J.C.S.*, 1896, 69, 1511).*

Condensation of cyclohexanone and 4-methylcyclohexanone with morpholine hydrochloride and aqueous formaldehyde solution to the hydrochlorides of the bases (V) and (VI) was readily effected by a method similar to that described by Mannich and Braun (*Berichte*, 1920, 53, 1875). Each of these ketonic bases could be reduced



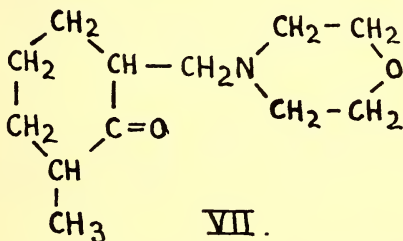
V.



VI.

to the corresponding alcohol by application of Ponndorff's method — treatment with aluminium isopropylate in absolute isopropyl alcohol. Both products were oily, being probably mixtures of stereoisomers, but from each crystalline hydrochlorides of the benzoic and p-nitrobenzoic esters could be readily prepared.

2-Methylcyclohexanone was induced to react with morpholine hydrochloride and paraformaldehyde by heating at 110° for two hours in cyclohexanol. The resulting hydrochloride of 2-methyl-6-morpholinomethylcyclohexanone (VII) was a colourless crystalline hygroscopic substance. The free base could be distilled undecomposed

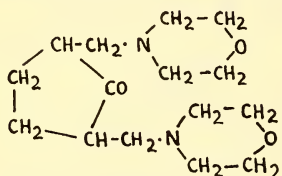


VII.

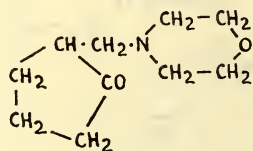
* After the work described in this paper had been completed there appeared a paper by Mannich and Fourneau in the *Berichte der deutschen chemischen Gesellschaft* in which were described almost exactly similar experiments, starting, however, from the free base dimethylaminobutanone and malonic ester, and cyclisation to dihydroresorcinol was effected with sodium ethoxide under mild conditions (*Ber.*, 1938, 71, 2090).

in vacuo, and crystallised in needles melting at 50°. It could be readily reduced by Ponndorff's method to the corresponding alcohol, from which the hydrochloride of the p-nitrobenzoic ester could be obtained crystalline.

When cyclopentanone was heated in alcoholic solution with morpholine hydrochloride and paraformaldehyde the main product of the reaction was the dihydrochloride of 2:5-dimorpholinomethylcyclopentanone (VIII) together with a small amount of the hydrochloride of 2-morpholinomethylcyclopentanone (IX).



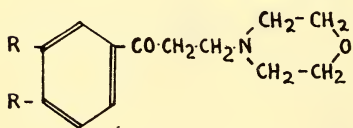
VIII.



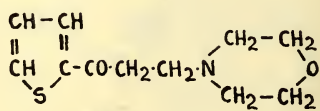
IX.

The hydrochloride of (IX) was the main product of reaction when cyclopentanone was reacted with morpholine hydrochloride and aqueous formaldehyde solution. Attempts to reduce (IX) to the corresponding alcohol by Ponndorff's method proved abortive.

The formation of "Mannich" ketonic bases from aryl alkyl ketones such as acetophenone has been described by Mannich and Lammering (*Berichte*, 1922, 55, 3510). We have found that under similar conditions, acetophenone, acetoveratrone, and α -acetothienone react readily with morpholine hydrochloride and paraformaldehyde to yield the hydrochlorides of the bases (X), (XI), and (XII) respectively.



X. (R = H)

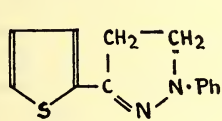
XI. (R = OCH₃)

XII.

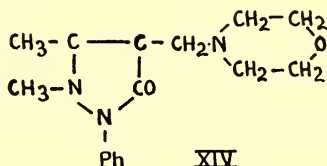
Each of these bases reacts readily with phenylhydrazine to give a crystalline pyrazoline of the type described previously by Mannich and Bauroth (*Berichte*, 1924, 57, 1108) and by Jacob and Madinaveitia (*J.C.S.*, 1937,

1929). It is worthy of comment here that the pyrazoline (XIII) from the base (XII) could not be isolated by Levvy and Nisbet (*J.C.S.*, 1938, 1053) from the Mannich bases prepared from α -acetothienone, formaldehyde, and piperidine or dimethylamine.

It is also worth recording that antipyrine reacts readily with formaldehyde solution and morpholine hydrochloride to give the highly crystalline morpholinomethylantipyrine (XIV) (cf. Mannich and Kater, *Arch. Pharm.*, 1919, 257, 18).



XIII.



XIV.

Finally, it should be noted that several of the substances described in the experimental section show definite local anæsthetic action. Of these, the most powerful effect was observed with the hydrochloride of the benzoate of morpholinobutanol. The hydrochloride of the p-nitrobenzoate of the same base was also definitely active though not so powerfully. A fairly strong action was also observed with the hydrochloride of β -morpholinoethylphenyl ketone. The hydrochlorides of the benzoates and p-nitrobenzoates of morpholinomethylcyclohexanol and the morpholinomethylmethylcyclohexanols showed only mild local anæsthetic action.

EXPERIMENTAL.

1-Morpholinobutan-3-one (I).

Acetone (60 c.c.), morpholine hydrochloride (42 g.), paraformaldehyde (16.8 g.) and absolute alcohol (10 ml.) were heated together under reflux for six hours. The solid gradually disappeared and eventually a homogeneous solution was obtained. On shaking this set to a solid crystalline mass whilst still hot. The mass was cooled, and the crystals freed from excess acetone on a porous tile. Recrystallised from absolute alcohol, this *1-morpholinobutan-3-one hydrochloride* was obtained in pearly white plates which melted at 149°.

Found: C=49.0, H=8.6, N=7.3%; calculated for $C_8H_{16}O_2NCl$, C=49.3, H=8.3, N=7.2%.

Addition of alcoholic picric acid to an alcoholic solution of this hydrochloride led to precipitation of a yellow oily *picrate* which was induced to crystallise by long standing in contact with alcohol, from which solvent it was then recrystallised. It formed yellow prisms melting at 114° .

Found: N=14.1%; calculated for $C_{14}H_{18}O_9N_4$, N=14.5%.

The free base, 1-morpholinobutan-3-one was prepared from the crude hydrochloride after removal of excess acetone by making strongly alkaline and extracting with ether. After drying and removal of the solvent, the oily base was distilled *in vacuo*. It came over as a colourless oil (38 g.) with a strong "amine" odour at $116^{\circ}/20$ mm. Considerable decomposition occurred during the distillation and a pale yellow residual resin was left in the flask. The base itself was not analysed.

1-Morpholinobutan-3-ol (II).

A solution of 1-morpholinobutan-3-one (37 g.) in ether (500 ml.) was treated with aluminium turnings (52 g.) previously activated by immersion in 4% mercuric chloride solution, and then heated under reflux. Water (50 ml.) was added gradually to the boiling liquid over a period of five hours. Eventually the aluminium hydroxide was filtered off, well washed with ether, and these washings combined with the ethereal solution, which was then dried and the solvent removed. The residual oil was distilled *in vacuo*, coming over as a colourless oil (10 g.) at $95-100^{\circ}/2.5$ mm. The poor yield is probably attributable to adsorption on the aluminium hydroxide and imperfect elution therefrom. The base was not analysed as such. Treatment of its alcoholic solution with alcoholic picric acid led to separation of an oily *picrate*, which crystallised after standing for a day. It was very soluble in alcohol, and was recrystallised from water, being thus obtained in yellow needles melting at $142-144^{\circ}$.

Found: N=14.2%; calculated for $C_{14}H_{20}O_9N_4$, N=14.4%.

1-Morpholino-3-benzoyloxybutane Hydrochloride.

To a solution of (II) (3 g.) in chloroform (5 ml.) was added a solution of benzoylchloride (3 g.) in chloroform (5 ml.). Evolution of heat occurred, and the colour deepened. After standing overnight the solvent was removed. The viscous residue crystallised on standing,

or, better, on rubbing with ether. Recrystallised twice from acetone it formed colourless prisms melting at 152°.

Found: N=4.9%; calculated for $C_{15}H_{22}O_3NCl$, N=4.7%.

The *picrate*, recrystallised from alcohol, formed bright yellow needles melting at 147°.

Found: N=11.4%; calculated for $C_{21}H_{24}O_{10}N_4$, N=11.4%.

1-Morpholino-3-p-Nitrobenzoyloxybutane Hydrochloride.

To a solution of (II) (3 g.) in chloroform (5 ml.) was added a solution of p-nitrobenzoylchloride (3.9 g.) in the same solvent (7 ml.). After standing overnight the solvent was removed and the residue rubbed with ether. It soon solidified, and was recrystallised twice from acetone, being thus obtained in very faintly yellow prisms melting at 199°.

Found: N=8.6%; calculated for $C_{15}H_{21}O_5N_2Cl$, N=8.2%.

The *picrate*, sparingly soluble in alcohol, formed yellow crystals melting at 211°.

Found: N=12.8%; calculated for $C_{21}H_{23}O_{12}N_5$, N=13.0%.

Ethyl α -Carbethoxy- δ -Keto Caproate (III).

Methyl iodide (34 g.) was added to an ice-cold solution of (I) (37.5 g.) in dry ether, and the mixture allowed to stand overnight. A white crystalline precipitate (47 g.), which tended to become gummy, had then separated. The supernatant liquid was poured off, and the solid washed with dry ether. This methiodide was not readily soluble in cold absolute alcohol. To it was added a solution of sodio malonic ester (prepared by adding ethyl malonate (31.4 g.) to a cooled solution of sodium (4.5 g.) in absolute alcohol (150 ml.)), and the mixture was gently warmed on the water-bath with shaking until the methiodide had separated from the walls of the flask. The mixture was then gently refluxed for three hours. Sodium iodide separated when the mixture was then cooled. Most of the solvent was removed by distillation, water was added, and the solution extracted several times with ether. The combined ethereal extracts were dried, the solvent removed and the residual oil fractionated *in vacuo*. Unchanged malonic ester (8.8 g.) came over first, and then a fraction

(9 g.) boiling at 157-158°/22 mm. When redistilled it boiled at 162-164°/26 mm.

This product gave no colour with ferric chloride solution, and is apparently not a β -diketone, or β -keto ester. Cyclisation to a dihydroresorecylic ester had therefore not occurred.

Found: C=57.2, H=7.5%; calculated for $C_{11}H_{18}O_5$, C=57.4, H=7.8%.

The substance is therefore, probably, the open-chain ethyl α -carbethoxy- δ -ketocaproate. When treated with aqueous-alcoholic semicarbazide acetate it readily yielded a *semicarbazone*, which formed flat colourless plates when recrystallised from a mixture of petroleum ether and alcohol, m.p. 118°.

Found: N=14.7%; calculated for $C_{12}H_{21}O_5N_3$, N=14.6%.

The *dinitrophenylhydrazone*, which came down with some difficulty owing to its ready solubility in alcohol, was recrystallised from petroleum ether and thus obtained in flat orange plates which melt at 55°.

Found: N=13.6%; calculated for $C_{17}H_{22}O_3N_4$, N=13.7%.

Attempts to effect cyclisation of this ester with alcoholic sodium ethoxide led only to formation of a viscous product which decomposed on attempted distillation *in vacuo*. Further proof of the constitution of the ester was obtained by its hydrolysis and decarboxylation to γ -acetylbutyric acid. When it was treated with 20% aqueous sodium hydroxide solution it went into solution, and after standing for some hours, then acidifying and exhaustively extracting with ether, there was isolated from this solution a viscous brown oil with acidic properties. When heated to 150-160° this lost carbon dioxide, leaving an oil which distilled at 150°/24 mm. There could be obtained from this oil with aqueous semicarbazide acetate a *semicarbazone* which crystallised in gleaming colourless needles from water and melted at 173°. This is the melting point recorded for the semicarbazone of γ -acetylbutyric acid by Bentley and Perkin (*J.C.S.*, 1896, 69, 1511).

2-Morpholinomethyl Cyclohexanone (V).

Cyclohexanone (49 g.; $\frac{1}{2}$ mol.), morpholine hydrochloride (13 g.; 1/10th mol.), and formaldehyde solution (9 g. of 40%) were gently warmed and vigorously shaken together.

After about 10 minutes some heat was evolved and eventually a homogeneous liquid was obtained. This was heated at 100° for a further five minutes, then allowed to cool. Finally, water (50 ml.) was added, and after vigorous shaking the upper layer of excess cyclohexanone removed. After two further extractions with ether the aqueous layer was evaporated *in vacuo*, a colourless crystalline deposit (24 g.) being obtained. Recrystallised from ethyl alcohol, this *2-morpholinomethylcyclohexanone hydrochloride* formed colourless prismatic needles melting at 128°.

Found: N=6.2%; calculated for $C_{11}H_{20}O_2NCl$, N=6.0%.

The *picrate* was readily soluble in hot alcohol but only sparingly soluble in cold, and crystallised in brilliant yellow needles melting at 135°.

Found: N=13.5%; calculated for $C_{17}H_{22}O_8N_4$, N=13.7%.

The free base (V) was readily obtained from a concentrated aqueous solution of the hydrochloride by making strongly alkaline and then extracting with ether. After drying and removal of the solvent the base distilled as a colourless oil at 145-147°/5.5 mm.

2-Morpholinomethylcyclohexanol (Va).

2-Morpholinomethylcyclohexanone (16 g.) was dissolved in absolute isopropyl alcohol (50 ml.) in a distilling flask and a solution of aluminium isopropoxide (12.5 g.) in isopropyl alcohol (75 ml.) added. This solution was kept gently boiling for five hours, the acetone formed in the reaction distilling over with some isopropyl alcohol. More isopropyl alcohol was added as required during the reaction. The presence of acetone in the distillate was shown by the formation of its D.N.P. When reduction was apparently complete, the isopropyl alcohol was removed as completely as possible by distillation, and the residue was treated with sodium hydroxide solution. The liberated base was taken up and dried in ether. After removal of the solvent it was distilled *in vacuo*, coming over between 120° and 128° at 1.8 mm. (8 g.).

This product was, most probably, a mixture of stereoisomers. It gave an oily picrate which could not be induced to crystallise.

2-Morpholinomethyl-1-Benzoyloxycyclohexane Hydrochloride.

A solution of the benzoylchloride (1 g.) in a little chloroform was added to a solution of the base (Va) (1 g.) in chloroform (5 ml.). The solution turned brown and heat was evolved. After standing overnight the chloroform was evaporated and the residue induced to crystallise by rubbing with ether. Recrystallised from acetone, it came out in colourless prisms melting at 211°.

Found: N=4.0%; calculated for $C_{19}H_{27}O_3NCl$, N=4.1%.

2 - Morpholinomethyl - 1 - p - Nitrobenzoyloxycyclohexane Hydrochloride.

Prepared from (Va) and p-nitrobenzoyl chloride in a manner similar to that described for the benzoic ester, this ester hydrochloride was recrystallised from a mixture of acetone and alcohol and was obtained in colourless prisms melting at 233°.

Found: C=55.5, H=6.7, N=7.1%; calculated for $C_{19}H_{26}O_5N_2Cl$, C=56.2, H=6.9, N=7.3%.

2-Morpholinomethyl-4-Methyl Cyclohexanone (VI).

A mixture of morpholine hydrochloride (12.4 g.), formaldehyde solution (9 g. of 40%), and 4-methylcyclohexanone (56 g.; excess) was warmed on the water-bath, and shaken for about 10 minutes until reaction commenced. Reaction proceeded with evolution of heat, and was finally completed by warming on the water-bath for a further 10 minutes. The homogeneous solution separated into two layers on cooling. The mixture was shaken out with water (50 ml.) and the aqueous extract freed from traces of methyl cyclohexanone with ether. The aqueous extract was then evaporated to dryness in a vacuum desiccator, a crystalline mass of *2-morpholinomethyl-4-methylcyclohexanone hydrochloride* being left. This was recrystallised from acetone, and then from a mixture of acetone and alcohol, and thus obtained in colourless prisms melting at 145°.

Found: C=58.4, H=9.3%; calculated for $C_{12}H_{22}O_2NCl$, C=58.2, H=8.9%.

The free base, liberated from a solution of the hydrochloride with alkali, washed and dried in ether and then distilled *in vacuo* came over at 131-132°/2.2 mm. as a colourless oil.

The *picrate*, thrice recrystallised from alcohol, formed bright yellow needles melting at 139°.

Found: N=12.9%; calculated for $C_{18}H_{24}O_9N_4$, N=12.7%.

2-Morpholinomethyl-4-methyl Cyclohexanol (VIa).

The keto base (VI) (9 g.) was reduced by the Ponndorff method with aluminium isopropoxide (6 g.) in isopropyl alcohol, the distillation being continued for three hours. Isolated by the method described for (Va) it was obtained as a colourless fairly viscous oil (7.5 g.) boiling at 135-137°/2 mm. A crystalline picrate could not be obtained from it.

2-Morpholinomethyl-4-Methyl-1-Benzoyloxycyclohexane Hydrochloride.

Obtained by a method similar to that described for the benzoic ester hydrochloride of (Va) this substance was obtained, after two recrystallisations from acetone, in colourless crystals melting at 228-230°.

Found: N=3.6%; calculated for $C_{19}H_{28}O_3NCl$, N=4.0%.

2-Morpholinomethyl-4-Methyl-1-p-Nitrobenzoyloxycyclohexane Hydrochloride.

Obtained in chloroform solution by interaction of (VIa) (1 g.) and p-nitrobenzoylchloride (1 g.), this substance was isolated as a syrup by removal of the solvent but crystallised after long contact with ether. After recrystallisation from a mixture of acetone and alcohol, a colourless crystalline solid melting at 242-244° was obtained.

Found: N=7.3%; calculated for $C_{19}H_{27}O_5N_2Cl$, N=7.0%.

2-Methyl-6-Morpholinomethyl Cyclohexanone (VII).

2-Methylcyclohexanone (40 g.; 2 mols.), morpholine hydrochloride (20 g.; 1 mol.) and paraformaldehyde (6.5 g.; 1.2 mols.) were heated together in cyclohexanol (100 g.) at 110° for two hours. After cooling the mixture was shaken out with water, and the aqueous extract freed from traces of methyl cyclohexanone and cyclohexanol with ether. It was then made alkaline with sodium hydroxide solution and the base collected with ether and eventually distilled *in vacuo*. It came over undecomposed

at 130°/1.8 mm., and after standing overnight crystallised out in colourless needles melting at 48-50°. The *picrate*, twice recrystallised from alcohol, formed long yellow needles melting at 118°.

Found: N=12.6%; calculated for $C_{18}H_{24}O_9N_4$, N=12.7%.

2-Methyl-6-Morpholinomethyl Cyclohexanol (VIIa).

The keto base (VII) (7 g.) was reduced with aluminium isopropoxide (4 g.) according to Ponndorff's method, as described for (V). The base was obtained as a colourless viscous oil boiling at 137-138°/2.3 mm. It gave an oily *picrate*. The hydrochloride of the benzoic ester, obtained in the usual manner, was an uncrystallisable oil. However, *2-methyl-6-morpholinomethyl-1-p-nitrobenzoyloxy-cyclohexane hydrochloride* was obtained in colourless needles melting at 237° after several crystallisations from a mixture of acetone and alcohol.

Found: N=7.0%; calculated for $C_{19}H_{27}O_5N_2Cl$, N=7.0%.

Condensation of Cyclopentanone with Formaldehyde and Morpholine Hydrochloride.

(A) *2-Morpholinomethylcyclopentanone (IX)*. Morpholine hydrochloride (12.4 g.; 0.1 mol.), formaldehyde solution (8 g. of 40%; 0.1 mol.), and cyclopentanone (42 g.; 0.5 mol.) were warmed together on the water-bath, with shaking until reaction commenced (five to ten minutes). Heating was discontinued and the reaction proceeded to completion of its own accord, a small amount of crystalline material separating towards the end. After cooling the mixture was shaken out with water (50 ml.), and the *hydrochloride of 2-morpholinomethylcyclopentanone* recovered from the aqueous extract by the usual method. The crude solid (19.5 g.) was taken up in boiling alcohol, the solution being filtered from a small amount (2 g.) of insoluble material (A), and allowed to crystallise after concentrating and cooling. It formed colourless prisms, melting at 137°.

Found: C=54.5, H=8.2%; calculated for $C_{10}H_{18}O_2NCl$, C=54.7, H=8.2%.

The *picrate* of the base (X), precipitated from an alcoholic solution of the hydrochloride by saturated alcoholic picric acid, after recrystallisation from alcohol formed yellow needles melting at 130°.

Found: N=13.6%; calculated for $C_{16}H_{20}O_3N_4$, N=13.6%.

The free base (IX) was recovered from the hydrochloride in the usual way and was obtained as a colourless oil boiling at 115-118°/2 mm. An attempt to reduce it to 2-morpholinomethylcyclopentan-1-ol by Ponndorff's method led to formation of an oil which broke down on distillation *in vacuo*, giving off morpholine.

(B) 2:5-Dimorpholinomethylcyclopentanone (VIII). Refluxing together cyclopentanone (21 g.), morpholine hydrochloride (31 g.), paraformaldehyde (9 g.) and absolute alcohol (20 ml.) for several hours led to the gradual separation of a white crystalline substance. After cooling this was collected and boiled with alcohol, in which it was very sparingly soluble. It was found to be insoluble in such solvents as benzene, dioxane, ethyl acetate, acetone and chloroform, but was readily soluble in water. Recrystallised from aqueous alcohol, it formed colourless needles melting at 195°, identical with the product (A) obtained as a by-product in the preparation of (IX).

Found: C=50.8, H=8.1%; calculated for $C_{15}H_{28}O_3N_2Cl_2$, C=50.7, H=7.9%.

The substance was thus the *dihydrochloride of 2:5-dimorpholinomethylcyclopentanone*.

The *picrate*, precipitated from alcohol solution, in which it is very sparingly soluble, was recrystallised from a large volume of alcohol. It formed bright yellow crystals melting at 152°.

Found: N=14.9%; calculated for $C_{27}H_{32}O_{17}N_8$, N=15.1%.

β-Morpholinoethylphenyl Ketone (X).

During the course of 30 minutes, acetophenone (24 g.) was gradually added to a boiling mixture of morpholine hydrochloride (26 g.), paraformaldehyde (9 g.) and absolute alcohol (60 ml.). A further quantity of paraformaldehyde (6 g.) was then added and the heating continued for a further 20 minutes. After filtration whilst still hot, the liquid separated into two layers on cooling. Eventually crystallisation commenced and it was possible to recover the hydrochloride of (X) (14 g.) by filtration. Heating of the mother liquor (still in two layers) until most of the alcohol had evaporated, followed by cooling and seeding led to separation of much more of the hydrochloride of

(X), the final yield being excellent. Recrystallised from absolute alcohol, the product was obtained in beautifully crystalline white needles melting at 177°.

Found: C=61.0, H=7.6%; calculated for $C_{13}H_{18}O_2NCl$, C=61.1, H=7.1%.

The *picrate* of (X) readily separated from alcoholic solution in yellow prisms, melting at 194°.

Found: N=12.8%; calculated for $C_{19}H_{20}O_9N_4$, N=12.5%.

The free base could readily be recovered as an oil from an aqueous solution of the hydrochloride, but it was not distilled, owing to the marked tendency observed by Mannich (*Berichte*, 1922, 55, 3510) of similar bases to decompose on attempted distillation. An attempt to reduce it by Ponndorff's method led to no isolable amino alcohol.

Heating of the base (X) with phenylhydrazine at 100° for several hours, or refluxing it with excess phenylhydrazine in alcoholic solution led to ready formation of the 1:3-diphenylpyrazoline melting at 153° previously described by Jacob and Madinaveitia (*J.C.S.*, 1937, 1929).

β-Morpholinoethyl-2-Thienyl Ketone (XII).

2-Acetylthiophene (30 g.) was added gradually over 30 minutes to a boiling mixture of morpholine hydrochloride (30 g.), paraformaldehyde (12 g.) and absolute alcohol (40 ml.) and then concentrated hydrochloric acid (0.5 ml.) was added and boiling continued under reflux for 20 minutes. Paraformaldehyde (3 g.) was added and refluxing continued for a further 15 minutes, when the contents of the flask solidified. After cooling, the solid was collected and recrystallised from alcohol, being thus obtained in nacreous plates (30 g.) melting at 194°.

Found: N=5.2%; calculated for $C_{11}H_{16}O_2NSCl$, N=5.0%.

It was thus the *hydrochloride of β-morpholinoethyl-2-thienyl ketone*. The *picrate* of XII was readily obtained from an alcoholic solution of the hydrochloride with alcoholic picric acid. Recrystallised from a mixture of alcohol and nitrobenzene it formed fine bright yellow needles melting at 189-190°.

Found: N=12.4%; calculated for $C_{17}H_{18}O_9N_4S$, N=12.3%.

The base (XII) was readily obtained as an oil which was not distilled.

1-Phenyl-3- α -Thienyl-Pyrazoline (XIII).

β -Morpholinoethyl α -thienyl ketone (XII; 3 g.) and phenylhydrazine (1.5 g.) were refluxed with ethyl alcohol (10 ml.) for two hours. The oil obtained by pouring into water was rubbed with dilute acetic acid, washed with water and then rubbed with alcohol, when it solidified. Recrystallised from alcohol it was obtained in pale yellow needles melting at 103°.

Found: N=12.3%; calculated for C₁₃H₁₂N₂S, N=12.3%.

Shaking of this solid substance with ether, ligroin, or petroleum ether imparted a blue fluorescence to these liquids. With concentrated sulphuric acid it gave a deep blue colour, whilst with concentrated nitric acid the colour was deep violet.

 β -Morpholinoethyl-3 : 4-Dimethoxyphenyl-Ketone (XI).

Acetoveratrone (36 g.) was added during half an hour to a boiling solution of morpholine hydrochloride (24.7 g.) paraformaldehyde (10 g.) and absolute alcohol (30 ml.). Concentrated hydrochloric acid (0.75 ml.) was then added and refluxing continued for 15 minutes. Two layers soon appeared, the lower layer gradually increasing in volume until the solution was again almost homogeneous. On cooling the *hydrochloride of (XI)* crystallised out. After collection and recrystallisation from boiling ethyl alcohol, in which it is but sparingly soluble, it was obtained in colourless prisms (35 g.) melting at 192°.

Found: N=4.5%; calculated for C₁₅H₂₂O₄NCl, N=4.4%.

The *picrate*, precipitated from an alcoholic solution of the hydrochloride, crystallised from a mixture of alcohol and nitro-benzene in yellow needles melting at 165°.

Found: N=11.0%; calculated for C₂₁H₂₄O₁₁N₄, N=11.0%.

The free base, (XI), was obtained by basification of an aqueous solution of the hydrochloride. Recrystallised from alcohol it formed colourless prisms melting at 129°.

Found: N=5.2%; calculated for C₁₅H₂₁O₄N, N=5.0%.

1-Phenyl-3-(3' : 4'-Dimethoxyphenyl)-Pyrazoline (XV).

A solution of the base (XI) (2 g.) and phenylhydrazine (1 g.) in absolute alcohol (10 ml.) was heated under reflux for an hour. On cooling the pyrazoline (XV) crystallised.

It was collected and recrystallised from alcohol, forming pale yellow needles melting at 130° .

Found: N=9.9%; calculated for $C_{17}H_{18}O_2N_2$, N=10.0%.

Solutions of this substance showed a characteristic blue fluorescence.

Morpholinomethyl Antipyrine (XIV).

Antipyrine (5 g.), morpholine hydrochloride (3.3 g.) and 40% formaldehyde solution (2.2 g.) were mixed in water and allowed to stand for 24 hours. The solution was then extracted with chloroform to remove unchanged antipyrine, made alkaline and again extracted with chloroform. After drying and removal of the solvent from this second extract, a crystalline product (6 g.) was obtained, which when recrystallised from ethyl acetate formed beautiful colourless flat prisms melting at 131° .

Found: C=67.1, H=7.8%; calculated for $C_{15}H_{21}O_2N_3$, C=66.9, H=7.3%.

The *picrate*, precipitated from alcohol and then recrystallised from the same solvent formed beautiful orange-yellow needles melting at 190° .

Found: N=16.6%; calculated for $C_{21}H_{24}O_9N_6$, N=16.3%.

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A CHEMICAL EXAMINATION OF THE FRUIT OF
PITTOSPORUM UNDULATUM.By JOHN W. CORNFORTH, B.Sc.,
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(Manuscript received, November 21, 1938. Read, December 7, 1938.)

The fruit of *Pittosporum undulatum* Ventenat, the "Mock Orange", was examined by Threlfall (*J. Proc. Roy. Soc. N.S.W.*, 1895, 29, 456), but no conclusions were drawn by this worker as to the chemical nature of any of its constituents. A glycosidic substance, pittosporine, was isolated from the bark and fruits by some earlier workers, but was not studied in great detail (Maiden, "Useful Native Plants of Australia", 1889 Edn., p. 199). The essential oil of the fruit was investigated by Power and Tutin (*J.C.S.*, 1906, 89, 1083), who found it to consist principally of limonene and pinene.

We have now re-examined the non-volatile constituents of the fruit, by extracting the ground dried material successively with ether and hot dilute alcohol.

The ethereal extract of the fruit consisted chiefly of fats. The portion of the extract remaining unattacked after saponification with alcoholic soda solution was found to contain two crystalline substances. The first had a melting point of 51-52° and was present in too small a quantity for identification; the second was identified as the paraffin pentatriacontane, m.pt. 73-75°.

The alcoholic extract of the fruit on evaporation left a brown amorphous powder, which was intensely irritating to the nose and throat when inhaled, and dissolved in water to give a strongly frothing solution. These properties indicated the presence of a saponin. When a solution of the material was hydrolysed by hot dilute hydrochloric acid, a deep red colour gradually appeared. The red substance could be extracted by means of amyl alcohol, and colour reactions showed it to be an anthocyanidin. Thus the presence of a leuco-anthocyanin, as well as a saponin, was indicated.

It was not found possible, despite various attempts, to separate these two constituents of the alcoholic extract. It was decided, therefore, to hydrolyse the entire extract, and to examine separately the products of hydrolysis.

A portion of the evaporated extract was dissolved in water and precipitated with calcium chloride. The precipitate thus obtained was rich in leuco-anthocyanin. It was hydrolysed with aqueous-alcoholic hydrochloric acid, and the anthocyanidin worked up and examined after the method of Robinson and Robinson (*Biochem. J.*, 1931, 25, 1687). It was identified as cyanidin.

Another portion of the alcoholic extract was hydrolysed with dilute aqueous-alcoholic hydrochloric acid. On removal of the alcohol, a mixture of sapogenin and anthocyanidin separated out. The *sapogenin* was extracted from this mixture by means of chloroform, and purified by repeated crystallisation from alcohol. It formed colourless platelets, m.pt. 308-310°, $[\alpha]_D^{20}$ 27.8°, and yielded a crystalline *acetate*, m.pt. 252-254°. On the basis of analyses and molecular weight determinations, we have assigned to the sapogenin the formula $C_{30}H_{50}O_7$. No substance resembling it has previously been reported, and we therefore propose for it the name *pittosapogenin*.

The sugars liberated by hydrolysis of the crude extract were also examined. They were found to be glucose and galactose, along with a little mannose. Pentoses, glycuronic acid and ketoses were absent. We found that the separation of glucose and galactose by means of methyl phenylhydrazine, as described by van der Haar (*Anleitung zur Nachweis, zur Trennung etc. . . der Monosaccharide*, 1920) was greatly improved by allowing the galactose methylphenylhydrazone to crystallise out for two days in the ice-chest, instead of six hours at room temperature. By adopting this procedure the glucosazone formed in the next step is readily purified.

The investigation is one of a series being made on the saponins and allied constituents of Australian plants. When further supplies of *Pittosporum* fruit become available, we shall attempt to isolate the saponin which they contain, and to determine as far as possible its chemical constitution.

EXPERIMENTAL.

Extraction of the Fruit. The fruit was ground and dried in a vacuum oven at 60°. The dried material (1 kg.) was

boiled up twice with ether (2 litres each time) and after each extraction well washed on the filter with fresh ether. The residue was then extracted twice with 50% alcohol (6 litres in all).

Examination of the Ethereal Extract. The orange-coloured solution (volume 5 litres) was evaporated, and the resultant thick syrup refluxed for four hours with N-alcoholic sodium hydroxide (500 ml.). The alcohol was then evaporated, water being added from time to time to replace it, and the resulting dark aqueous solution was extracted with ether in a continuous extraction apparatus. The extract was dried and evaporated, and the residue distilled *in vacuo*. A small fraction passed over at 160-170°/1.5 mm. and solidified in the receiver; a second and larger fraction, which also crystallised, distilled at 220-230°/1.5 mm. The first fraction was recrystallised from alcohol, and formed microscopic leaflets, m.pt. 51-52°, but as only 10 mg. of the substance was obtained its further investigation was abandoned. The higher boiling fraction (2 g.) on crystallisation from ethyl acetate formed colourless leaflets, m.pt. 73-75°. This substance was neutral, did not decolourise bromine in carbon tetrachloride, did not dissolve in warm concentrated sulphuric acid, and was unaffected by boiling with acetic anhydride. These properties point to a paraffin, and the melting point and boiling point of the substance identify it with penta-triacontane.

The acids liberated by the saponification were isolated by acidifying the aqueous alkaline solution remaining from the ether extraction, and shaking out with ether. They formed a semi-solid mass, and contained a small proportion of material volatile in steam. They were not further examined.

Examination of the Alcoholic Extract. The extract evaporated on the water-bath, and left a brown powder (80 g.). Its properties have been described above. It was subjected directly to hydrolysis and the products examined.

Identification of the Anthocyanidin. A portion of the evaporated extract (1 g.) was dissolved in water (20 ml.) and a little calcium chloride solution added. The resulting precipitate was collected and hydrolysed on the water-bath with 10% aqueous-alcoholic hydrochloric acid. The alcohol was next removed and the anthocyanidin worked up as

described by Robinson and Robinson (*loc. cit.*). The partition and colour tests gave the following results :

(i) The anthocyanidin gave a bright red solution in amyl alcohol ; addition of sodium acetate changed the colour to reddish-violet. When ferric chloride was added to the solution either with or without previous addition of sodium acetate, a pure blue colour was produced.

(ii) A solution of the anthocyanidin in 1% HCl, when shaken with the "cyanidin reagent", gave the characteristic rose-pink colour in the upper layer.

(iii) The anthocyanidin was recovered without apparent loss from the "oxidation test".

(iv) The "delphinidin reagent" did not completely extract the anthocyanidin from dilute solution in 1% HCl.

The results of these tests indicated that the substance was cyanidin.

Isolation of the Sapogenin. The remainder of the powder from the evaporation of the alcohol extract was hydrolysed by heating for six hours with 50% alcohol (2 l.) containing 2½% of hydrochloric acid. The alcohol was then removed, and the insoluble solid filtered, washed with water, dried and extracted (Soxhlet) with chloroform. On evaporation of the solvent a dark gum remained, which was taken up in alcohol and allowed to stand in a desiccator for a week. A partly crystalline solid separated (10 g.). It was recrystallised eight times from alcohol (the process was tedious, for the substance dissolved and separated very slowly) and finally obtained in beautiful, colourless, rectangular platelets, melting with some previous softening at 308-310°.

Found : C=68.6, H=9.7% ; calculated for $C_{30}H_{50}O_7$, C=68.9%, H=9.6%.

The substance contained no solvent of crystallisation, no loss of weight being observed on heating at 110° in a vacuum over phosphoric oxide. It was optically active, $[\alpha]_D^{20}$ 27.8°, in a mixture of chloroform and methanol. It was sparingly soluble in most organic solvents. Like many triterpenoid compounds, it gave a purplish-red Liebermann-Burchard reaction.

Acetylation of Sapogenin. The sapogenin (0.3 g.) was dissolved in anhydrous pyridine (7 ml.) and freshly distilled acetic anhydride (2.5 ml.) added. After standing overnight the solution was poured into water and extracted with ether. The ethereal solution was washed successively with dilute hydrochloric acid, sodium carbonate solution,

and water. It was then dried and evaporated. The product, a light yellow resin, was taken up in a little benzene, from which it crystallised in well-formed microscopic rhombic plates (0.15 g.) melting at 252-4°.

Found: C=67.1, H=8.6%; calculated for $C_{30}H_{48}O_5(CH_3COO)_2$, C=67.3, H=8.9%.

Found: M (ebullioscopic in benzene)=575, 600; calculated, M=606.

Examination of the Sugars. The mother liquor from the hydrolysis was extracted with amyl alcohol to remove dissolved anthocyanidin. The solution was then concentrated somewhat, and precipitated with lead acetate solution. Lead was removed from the filtrate by addition of sodium phosphate solution, and the neutralised filtrate (volume 500 ml.) examined for sugars. Tests for pentoses, methyl pentoses, glycuronic acid and ketoses were negative. The sugar solution gave a slight precipitate with phenylhydrazine acetate in the cold, and a larger precipitate with methylphenylhydrazine. This foreshadowed the presence of mannose and galactose.

A portion of the solution (40 ml.) was treated with phenylhydrazine acetate (1.5 g.) and the solution allowed to stand in the ice-chest for 24 hours. The precipitate was then collected and crystallised twice from water. It was then partly crystalline but the melting point was too indefinite and the quantity too small for positive identification with mannose phenylhydrazone. However, as mannose phenylhydrazone is the only hexose phenylhydrazone precipitable from aqueous solution, there is little doubt that a trace of mannose was present in the sugar mixture.

The filtrate from the phenylhydrazone was treated with an equal volume of alcohol, and benzaldehyde was added in amount equivalent to the phenylhydrazine used. The mixture was refluxed for an hour, the alcohol removed and the benzaldehyde phenylhydrazone filtered off. The solution was shaken out several times with ether, and then treated with methylphenylhydrazine (1 g.) and sufficient alcohol to give a clear solution. The solution was allowed to stand in the ice-chest for two days, when the separation of the crystalline precipitate was quite complete. When in another experiment the solution was allowed to stand for 6 hours at room temperature (the time cited by van der Haar, *loc. cit.*), then filtered and placed in the ice-chest for 24 hours, it was found that an appreciable amount of

substance separated during the second period. The hydrazone precipitate, after two crystallisations from 30% alcohol, melted at 189-190° and was therefore galactose methylphenylhydrazone.

The filtrate from the galactose derivative was now heated with phenylhydrazine acetate in excess. After cooling the crystalline osazone was collected and well washed on the filter with cold acetone. After three crystallisations from 30% alcohol it had m.pt. 205-6° and was identical with phenylglucosazone. The difficulty experienced by van der Haar (*loc. cit.*) in purifying the osazone is thus avoided by longer standing of the galactose methylphenylhydrazone to ensure complete separation.

A quantitative estimation of the sugars was not attempted, for it would have served no purpose. It was observed, however, that glucose was present in considerably larger amount than galactose.

ACKNOWLEDGMENTS.

The authors' thanks are due to Miss D. M. Little, B.Sc., for analyses ; to Mr. N. G. Hills, B.Sc., who kindly collected a supply of the fruit ; and to the University of Sydney for a Science Research Scholarship awarded to one of them (J.W.C.).

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THE GLYCOSIDE OF PERSOONIA SALICINA
FRUITS.

By JOHN W. CORNFORTH, B.Sc.

(Communicated by PROFESSOR J. C. EARL.)

(Manuscript received, November 21, 1938. Read, December 7, 1938.)

Persoonia salicina Pers. is a species of the genus commonly known as "geebungs", several members of which are known in this State. In season the plant bears clusters of bright green fruit, ovate in shape and generally 1-2 cm. long. The fruit is made up of a green outer rind enclosing a mass of white pulp, in which the stone is embedded. The fruit used in this investigation was collected in the Blue Mountains, N.S.W.

The fruit had an exceedingly bitter taste, and on keeping turned gradually black. It seemed probable in view of these properties that it contained a phenolic glycoside. By using a suitable method of extraction, the crude glycoside was obtained as a syrup, and purified through its crystalline acetyl derivative. The pure glycoside thus obtained was identical with arbutin.

Although arbutin occurs very frequently in plants, it is almost invariably accompanied by its monomethyl ether, methylarbutin. The separation of these two glycosides can be effected by tedious processes of fractional crystallisation, either of the mixed acetates or of the additive compound which arbutin forms with hexamethylenetetramine (Mannich, *Arch. Pharm.*, 250, 547; Macbeth, Mackay, *J.C.S.*, 1923, 123, 717). The glycoside of *Persoonia salicina*, however, appears to contain no methylarbutin, and its double melting point (163-164° and again at 198-199°) agrees well with that of the pure synthetic product (163-164° and again at 199-200°). *Persoonia salicina* may therefore be regarded as an excellent source of pure arbutin.

The fruit of *Persoonia pinifolia* R.Br., a closely related species, was also examined, but was found to contain no arbutin. If opportunity arises, an examination will be made of other species of "geebungs".

EXPERIMENTAL.

Preparation of the Crude Glycoside. A quantity of *Persoonia salicina* fruit was stoned and passed through a

mincer. The minced material (700 g.) was immediately extracted with hot alcohol (1 l.). After filtration the residue was boiled up with fresh alcohol (1 l.) and the united extracts evaporated *in vacuo*. The resulting thick syrup was taken up in water (400 ml.) and lead acetate solution added until no further precipitate appeared. The lead precipitate was centrifuged off, and the clear solution freed from lead ions by adding sodium phosphate solution and again centrifuging. Finally the solution was evaporated *in vacuo*, and the heating continued under vacuum until water was no longer expelled. A dark syrup (60 g.) remained.

Penta-acetyl Arbutin. A portion of the syrup (10 g.) was warmed with anhydrous pyridine (100 ml.) and acetic anhydride (40 ml.) for 15 minutes on the water-bath. The solution was then poured into water (500 ml.) and extracted with ether. The ethereal solution was washed successively with dilute hydrochloric acid, sodium carbonate solution and water, dried over sodium sulphate and evaporated. A thick oil remained which crystallised on standing. The crystals (4 g.) were collected and crystallised once from alcohol. In this way thin colourless needles were obtained, m.pt. 144–145° (Mannich, *loc. cit.*, gives 144–145° as the melting point of penta-acetyl arbutin). A further crystallisation did not affect the melting point.

Arbutin. The acetate (2 g.) was shaken with 5% baryta solution (90 ml.) for two days at room temperature. The acetate slowly dissolved. Carbon dioxide was then passed through the solution to precipitate excess barium as carbonate. The solution was filtered and concentrated to small bulk, when a mass of fine needles (1 g.) separated. After recrystallisation from water the glycoside melted at 163–164°, then solidified again as the temperature was raised, and melted again at 198–199°. The substance yielded pure hydroquinone (m.pt. 170°) on hydrolysis. The remainder of the crude glycoside syrup was induced to crystallise by seeding with the pure arbutin.

ACKNOWLEDGMENTS.

The author wishes to thank Miss V. May, B.Sc., for botanical advice; Professor J. C. Earl, D.Sc., Ph.D., for his interest in the work; and the University of Sydney for a Science Research Scholarship.

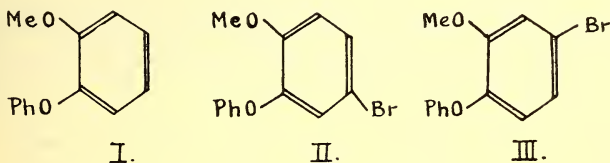
Department of Organic Chemistry,
University of Sydney.

THE BROMINATION OF 2-METHOXYDIPHENYL ETHER.

By FRANCIS LIONS, B.Sc., Ph.D.,
and ALAN M. WILLISON, M.Sc., A.A.C.I.

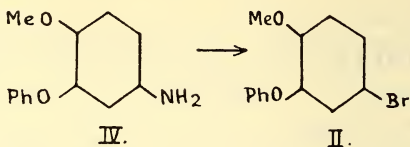
(Manuscript received, November 23, 1938. Read, December 7, 1938.)

It has been shown that 2-methoxydiphenyl ether (I) on nitration in glacial acetic acid yields only two products, 5-nitro-2-methoxydiphenyl ether and 4-nitro-2-methoxydiphenyl ether. (Lions and Willison, *J. and Proc. Roy. Soc. N.S.W.*, 1937-8, 71, 435.) It was therefore reasonable to anticipate that treatment of 2-methoxydiphenyl ether (I) with the equivalent amount of bromine for monosubstitution would yield a product containing mainly 5-bromo-2-methoxydiphenyl ether (II) and some 4-bromo-2-methoxydiphenyl ether (III).

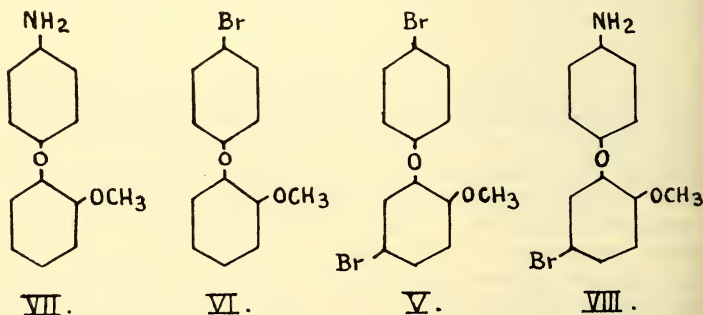


However, experiment has shown that it is not possible to obtain quantitative monosubstitution, and the colourless oily product obtained by bromination in glacial acetic acid at room temperature does not separate readily into well defined fractions on distillation. By collection of fractions boiling over ranges of approximately ten degrees, some separation of the mixture into its components can be effected. From fraction (A), b.pt. 192-203°/25 mm., unchanged 2-methoxydiphenyl ether (I), m.pt. 78°, was recovered; the fractions (B), b.pt. 203-210°/25 mm., (C), b.pt. 210-220°/25 mm., and (D), b.pt. 220-235°/mm., yielded in varying amounts 5-bromo-2-methoxydiphenyl ether (II), colourless prismatic needles melting at 71°, which was identified by comparison with an authentic

specimen prepared from 5-amino-2-methoxydiphenyl ether (IV) by Gattermann's method.

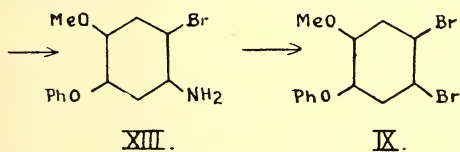
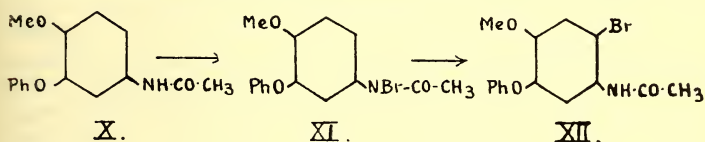


The fractions (E), boiling range 235-245°/25 mm., and (F), boiling range 245-250°/25 mm., yielded colourless crystalline plates, melting at 64°, of dibromomethoxydiphenyl ether and identical with the chief product of the reaction of (I) in glacial acetic acid with two molecules of bromine. This dibromo derivative was shown to be 4':5-dibromo-2-methoxydiphenyl ether (V) by its synthesis (a) by the bromination of 4'-bromo-2-methoxydiphenyl ether, (VI), in turn readily obtained from 4'-amino-2-methoxydiphenyl ether (VII); and (b) from 4'-amino-5-bromo-2-methoxydiphenyl ether, (VIII), by Gattermann's method. This latter substance was prepared by the method of Buchan and Scarborough (*J.C.S.*, 1934, 706) and was found to melt at 88° and not at 105° as stated by these authors. As 4'-amino-4:5-dibromo-2-methoxydiphenyl ether (XIV), which they also described, melts at 105-106°, it seems possible that they may have confused the specimens.

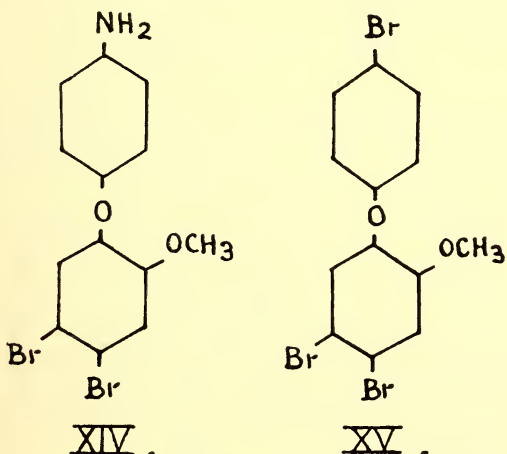


It was not the 4:5-dibromo-2-methoxydiphenyl ether (IX), which might have been expected. This latter substance was synthesised by the following method: 5-Acetylamino-2-methoxydiphenyl ether (X) brominated

readily to an intermediate substance melting at 158° , which may be a partial hydrobromide of 5-acetylbrom-amino-2-methoxydiphenyl ether (XI). This was very readily converted to 4-bromo-5-acetylamino-2-methoxydiphenyl ether (XII), by contact with water or hydroxylic solvents. This latter substance was hydrolysed with difficulty (cf. Simonsen and Rau, *J.C.S.*, 1918, 113, 782) to 4-bromo-5-amino-2-methoxydiphenyl ether (XIII), which was then converted by Gattermann's method to (IX).

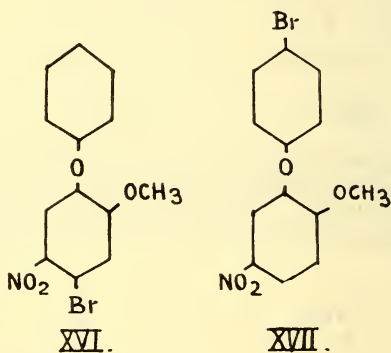


The attempted preparation of (IX) from 4'-amino-4 : 5-dibromo-2-methoxydiphenyl ether (XIV) by diazotisation and reduction with alkaline stannous chloride failed, apparently because of the stability of the amine to nitrous acid.



A tribromo derivative which formed pink-tinged needles melting at 131° was isolated from the residue (G) in the Claisen flask after removal of all products below $250^{\circ}/25$ mm. from the original bromination mixture. By analogy with the work of Buchan and Scarborough (*J.C.S.*, 1934, 705), this substance was assigned the constitution of 4 : 4' : 5-tribromo-2-methoxydiphenyl ether (XV).

A further yield of 5-bromo-2-methoxydiphenyl ether (II) was obtained by treating the residual oils from the fractions B, C, and D in glacial acetic acid with nitric acid ($d=1.42$). 5-Bromo-2-methoxydiphenyl ether (II) is not attacked by nitric acid in the cold, and any 4-bromo-2-methoxydiphenyl ether (III) or 4'-bromo-2-methoxydiphenyl ether (VI) present are probably nitrated and removed as 4-bromo-5-nitro-2-methoxydiphenyl ether (XVI) and 4'-bromo-5-nitro-2-methoxydiphenyl ether (XVII) respectively, although neither of these products could be isolated.

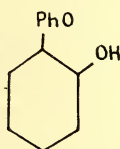


The oily product precipitated from the nitration mixture with water on distillation *in vacuo* gave a fraction boiling at $214-222^{\circ}/25$ mm., from which (II) could be induced to crystallise, leaving a residual yellow oil.

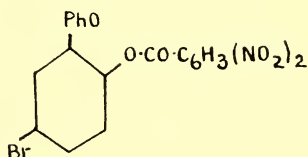
This readily reacted partially with piperidine, leaving a semi-crystalline mass of more unchanged (II), but no definite crystalline piperidino compound could be isolated.

Although 4-bromo-2-methoxydiphenyl ether (III), 4'-bromo-2-methoxydiphenyl ether (VI) and 4 : 5-dibromo-2-methoxydiphenyl ether (IX) could not be isolated from the products of bromination, the possibility of their presence in small amounts in the inseparable oils is not rigidly excluded.

If the bromination of 2-methoxydiphenyl ether is carried out in glacial acetic acid at 75° , the hydrobromic acid evolved causes some hydrolysis of the methoxy group so that phenols are obtained in addition to the above-mentioned products. 2-Hydroxydiphenyl ether (XVIII), m.pt. 106° , was isolated and 5-bromo-2-hydroxydiphenyl ether could also be separated as its 3:5-dinitrobenzoyl derivative (XIV), white microneedles melting at 102° .



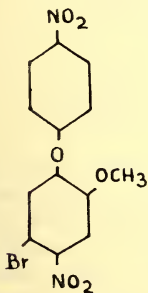
XVIII



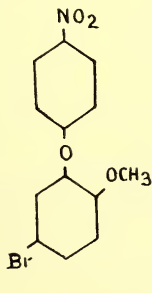
XIV

5-Bromo-2-methoxydiphenyl ether (II) reacts like a diphenyl ether and not like a catechol ether. It nitrates only with difficulty to give a dinitro derivative apparently substituted in the 4:4'-positions; it does not seem possible easily to obtain a mono-substituted nitro derivative by direct nitration.

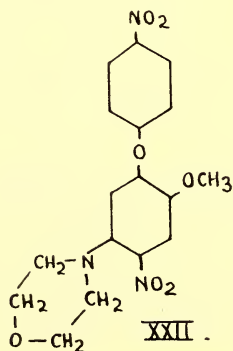
4:4'-Dinitro-5-bromo-2-methoxydiphenyl ether (XX) was obtained by the action of fuming nitric acid ($d=1.5$) on (II) in a mixture of glacial acetic acid and acetic anhydride, or by the action of concentrated nitric acid on (II) with gentle warming. It was also obtained from 4'-nitro-5-bromo-2-methoxydiphenyl ether (XXI) under similar conditions of nitration.



XX.



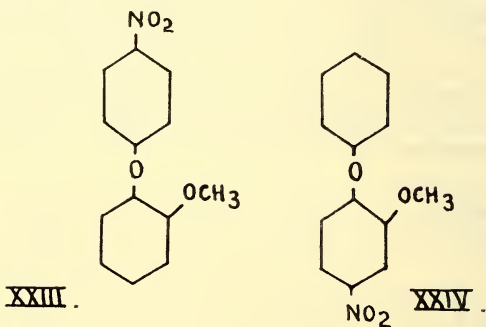
XXI.



XXII.

The orientation of the second nitro group in the 4 position was proved by the fact that (XX) reacted readily with piperidine (*cf.* Le Fevre and Turner, *J.C.S.*, 1927, 1113) and with morpholine (*cf.* Harradence and Lions, *J. and Proc. Roy. Soc. N.S.W.*, 1936, 70, 406). From the product of the reaction of morpholine on (XX) 5-morpholyl-4 : 4'-dinitro-2-methoxydiphenyl ether (XXII) was isolated.

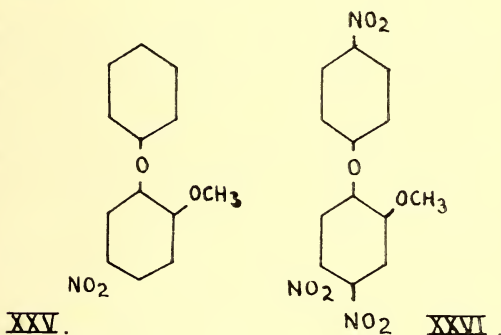
Buchan and Scarborough (*loc. cit.*) state that 5-chloro-4'-nitro-2-methoxydiphenyl ether on nitration yields a product in which the second nitro group is not ortho to the halogen as it does not react with piperidine. Unfortunately, no mention is made of their method of nitration, of the product so obtained, or its analysis, in their paper, nor in that of Scarborough and Sweeten (*J.C.S.*, 1934, 867), who cite this experiment. It is noteworthy that neither 4'-nitro-2-methoxydiphenyl ether (XXIII) nor 4'-nitro-5-bromo-2-methoxydiphenyl ether (XXI) react readily with piperidine, the nitro group in the 4'-position not being sufficiently powerful to activate the para aryloxy group (*cf.* Le Fevre, Saunders and Turner, *J.C.S.*, 1927, 1168). A nitro group in the 4-position is quite sufficient to cause this scission, which is extremely readily effected in the case of 4-nitro-2-methoxydiphenyl ether (XXIV) (Lions and Willison, *loc. cit.*).



The other positions for a nitro group which would give reactions with piperidine and morpholine would be the 2'- and the 6-positions. The 2'-position is excluded by the preparation of 2' : 4'-dinitro-5-bromo-2-methoxydiphenyl ether by Scarborough and Sweeten (*loc. cit.*) and the 6-position by analogy with the work of Gaspari (*Gazzetta*, 1896, 26, ii, 231) and Jones and Robinson (*J.C.S.*, 1917,

903) who by the nitration of 4-bromoveratrole obtained 4-bromo-5-nitroveratrole as a sole product.

In view of this reaction, the action of one molecule of bromine on 5-nitro-2-methoxydiphenyl ether (XXV) was studied. The sole product was 4'-bromo-5-nitro-2-methoxydiphenyl ether (XVII) obtained as glistening pale yellow leaflets melting at 150°. The same product was also obtained by the nitration of 4'-bromo-2-methoxydiphenyl ether (VI). This reaction forms a useful contrast with the reaction of 4-nitroveratrole with bromine to give 3-bromo-5-nitroveratrole (Jones and Robinson, *loc. cit.*). It would thus appear that after substitution in the 5-position 2-methoxydiphenyl ether ceases to act as a catechol ether, the position taken up by a second group being dependent upon the group already present in the 5-position and also on the entering group.



It has been previously shown that with an acetylamino group in the 5-position, nitration occurs in the 4-position (Lions and Willison, *loc. cit.*). A similar orientation for the acetylamino group has been assumed in the rearrangement of the 5-acetbromamino derivative (see above). With the bromine atom in the 5-position, further bromination occurs chiefly in the 4'-position and nitration leads to the formation of the 4 : 4'-derivative. With the nitro group in the 5-position, bromination occurs solely in the 4'-position. It is probably also worthy of comment that nitration of 2-methoxy-diphenyl ether can yield a trinitro derivative (Lions and Willison, *loc. cit.*), which from consideration of the nitration of the 5-bromo derivative discussed above is probably 4 : 4' : 5-trinitro-2-methoxydiphenyl ether (XXVI), a structure further supported by

the ease with which the trinitro derivative in question reacts with piperidine.

Finally, it should be recorded that 4-nitro-2-methoxydiphenyl ether (XXIV) (Lions and Willison, *loc. cit.*) has now been obtained in crystalline form as pale yellow, transparent, hexagonal blocks melting at 59°.

EXPERIMENTAL.

The Bromination of 2-Methoxydiphenyl Ether.

To a solution of 2-methoxydiphenyl ether (I) (40 g.) in glacial acetic acid (200 c.c.) was gradually added a solution of bromine (32 g.) in glacial acetic acid (40 c.c.). The reaction mixture was allowed to stand for 24 hours at room temperature, then gently heated till dilution with water of a test portion no longer gave any pink colour, when the whole was diluted with water, and the precipitated oil taken up in ether, washed with caustic soda solution and water, dried over anhydrous sodium sulphate and the solvent removed. The residual oil, distilled *in vacuo*, gave no definite boiling fractions. The fraction (A) boiling over the range 192-203°/25 mm. deposited colourless needles on cooling, which melted at 78° after recrystallisation from alcohol and were identical with 2-methoxydiphenyl ether (I). From the fractions (B), boiling range 203-210°/25 mm., (C), boiling range 210-220°/25 mm., and (D), boiling range 220-235°/25 mm., was gradually deposited a solid substance which crystallised from alcohol in colourless prismatic needles melting at 71° and later was shown to be 5-bromo-2-methoxydiphenyl ether (II); whilst the fractions (E), boiling range 235-245°/25 mm., and (F), boiling range 245-250°/25 mm., yielded a solid dibromo-derivative which was obtained from alcohol in colourless plates melting at 64°, identical with the product obtained by treating 2-methoxydiphenyl ether (I) with two equivalents of bromine, and shown to be 4':5-dibromo-2-methoxydiphenyl ether (V). The residue in the Claisen flask from the distillation was recrystallised from alcohol, from which it came down as prismatic needles melting at 131°. This substance was a tribromo-derivative, probably 4:4':5-tribromo-2-methoxydiphenyl ether (XV).

Found: Br=54.5%; calculated for C₁₃H₉O₂Br₃, Br=54.8%.

By further fractionation of the oils which were separated from the crystalline products of the bromination further yields of these products were obtained.

The total yields were as follows :

Unchanged 2-methoxydiphenyl ether	..	5 g.
Inseparable oil boiling below 205°/25 mm.	..	5 g.
5-bromo-2-methoxydiphenyl ether	..	16 g.
Inseparable oil boiling 205-222°/25 mm.	..	12 g.
Inseparable oil boiling 222-240°/25 mm.	..	4 g.
4' : 5-Dibromo-2-methoxydiphenyl ether	..	7 g.
Inseparable oil boiling above 240°/25 mm.	..	4 g.
4 : 4' : 5-Tribromo-2-methoxydiphenyl ether	..	1 g.

If the acetic acid solution after bromination is heated at 75° for several hours, the methoxy group is partially hydrolysed and the phenols thus formed may be recovered from the oily reaction product by extraction of its solution in ether with caustic alkali solution. By acidification of the alkaline solution the phenols are re-precipitated and may be extracted with ether, washed with water, dried, the solvent removed and then distilled *in vacuo*.

The fraction boiling over the range 194-200°/25 mm. crystallised on cooling and was recrystallised from light petroleum to give colourless needles melting at 106° and shown by comparison to be 2-hydroxydiphenyl ether (XVIII). The second fraction, boiling range 200-210°/25 mm., could not be induced to crystallise, so the 3 : 5-dinitrobenzoyl derivative was formed by the addition of an equal quantity of 3 : 5-dinitrobenzoyl chloride to the oil in the presence of aqueous caustic soda. The resulting pale yellow gum was extracted with alcohol and recrystallised from a benzene-petroleum ether mixture ; white micro needles, melting at 102°, of 5-bromo-2-(3 : 5-dinitrobenzoyl) oxydiphenyl ether (XIX) were thus obtained.

Found : N=6.1, Br=17.3% ; calculated for $C_{19}H_{11}O_7N_2Br$, N=6.1%, Br=17.4%.

Nitration of the Oily Residues from the Bromination.

To a solution of the oily fraction, boiling range 205-222°/25 mm. (12 g.), in glacial acetic acid (60 c.c.) was added nitric acid (D=1.42 ; 8 c.c.) in glacial acetic acid (20 c.c.). A red colour developed almost immediately. After allowing to stand for half an hour, water was added and the precipitated oil taken up in ether and washed with sodium hydroxide solution, when the sparingly soluble

salt of a nitrophenol separated. After washing several times with sodium hydroxide solution and water, then drying, the solvent was removed, leaving a red oil which was distilled *in vacuo*. No very definite fractions could be separated. The fraction, boiling range 214-222°/25 mm., was induced to deposit colourless needles, which were identified as unchanged 5-bromo-2-methoxydiphenyl ether (II), m.pt. 71°. The oily residual portion of this fraction was treated with piperidine as follows: the oil (3 g.) was refluxed for six hours with piperidine (10 c.c.) and the solution then cooled and diluted with water. The precipitated semi-crystalline oil was filtered off and the oil pressed out. The crystalline material was recrystallised from alcohol and came down as colourless needles melting at 71°, again found to be 5-bromo-2-methoxydiphenyl ether (II). No other definite crystalline product could be isolated.

The higher boiling fractions of the nitrated oil could not be separated into any particular products.

The combined alkaline extracts of the crude nitration product were freed from ether and acidified and the liberated phenol collected and recrystallised from aqueous alcohol. It came down in pale yellow needles melting at 154°. This phenol does not give any characteristic reaction with ferric chloride. Sodium fusion indicated the absence of any bromine. A nitrogen analysis on this substance showed the presence of 9.6% of nitrogen. A dinitrohydroxy methoxydiphenyl ether would contain 9.2% of nitrogen, and the product may conceivably be such a substance.

Synthesis of 5-Bromo-2-Methoxydiphenyl Ether.

5-Amino-2-methoxydiphenyl ether (IV) (Lions and Willison, *loc. cit.*) (2 g.) was heated with hydrobromic acid ($d=1.48$; 10 c.c.) and water (5 c.c.) and completely converted to its sparingly soluble hydrobromide. The mass was cooled to 0° and sodium nitrite (0.68 g.) in a little water was slowly added with stirring, the temperature being maintained below 5°. After the addition of the sodium nitrite solution, the reaction mass was allowed to stand for 30 minutes, filtered and poured into hydrobromic acid (30%; 20 c.c.) containing active copper powder. When the reaction mixture was carefully and slowly heated on a water bath the bromo compound separated as an oil around the copper. The reaction product was taken up in

ether, washed with alkali and water, dried, and after removal of the solvent distilled *in vacuo*. An oil (2 g.; 74% yield) distilled at 214-216°/25 mm. and was induced to crystallise on cooling. Recrystallised from alcohol, it was obtained in colourless prismatic needles melting at 71° alone or mixed with the bromo derivative, m.pt. 71°, obtained by the action of bromine on 2-methoxydiphenyl ether (I).

Found: Br=28.6%; calculated for $C_{13}H_{11}O_2Br$, Br=28.7%.

4'-Bromo-2-Methoxydiphenyl Ether (VI).

To 4'-amino-2-methoxydiphenyl ether (VII) (Buchan and Scarborough, *loc. cit.*; 9 g.) was added hydrobromic acid (33%; 75 c.c.) and the mixture cooled to 0°. Sodium nitrite (3.0 g.) was added slowly with stirring. After standing an hour, the diazonium salt solution was added to copper powder in hydrobromic acid at 0° and stirred vigorously. Nitrogen was evolved. After standing for an hour the mixture was carefully heated and stirred till the evolution of nitrogen ceased, then extracted with ether. The solvent was removed from the washed and dried extract and the residual oil distilled *in vacuo*. It boiled at 195-197°/15 mm. and came over as a colourless oil which solidified on scratching. It has a pleasant odour, similar to but more pronounced than the other monobromo compound (II) described. It was recrystallised from ethyl alcohol and obtained in needles melting at 38°. The yield was excellent.

Found: Br=25.7%; calculated for $C_{13}H_{11}O_2Br$, Br=28.7%.

4'-Amino-5-Bromo-2-Methoxydiphenyl Ether.

This substance was obtained in 80% yield from 4'-nitro-2-methoxydiphenyl ether (XXIII) by bromination followed by reduction, exactly as described by Buchan and Scarborough (*loc. cit.*), who gave the melting point as 105°. Our product melted sharply at 88°, and as 4'-amino-4:5-dibromo-2-methoxydiphenyl ether melts at 105-106° it seems possible that they may have confused the specimens.

Found: Br=27.1%; calculated for $C_{13}H_{12}O_2NBr$, Br=27.2%.

4' : 5-Dibromo-2-Methoxydiphenyl Ether (V).

2-Methoxydiphenyl ether (I) (10 g.) in glacial acetic acid (50 c.c.) was treated with bromine (16 g.) in glacial acetic acid (10 c.c.).

The reaction mixture was allowed to stand for 40 hours and was then heated at 100° for a few minutes. On dilution with water an oil separated, which was taken up, washed and dried in ether, and the solvent removed leaving a colourless oil. Practically all of this distilled over at 241-243°/25 mm. as a colourless oil which could readily be induced to solidify. Recrystallised from alcohol it was obtained in colourless plates melting at 64°.

(b) To 4'-bromo-2-methoxydiphenyl ether (VI) (1 g.) in glacial acetic acid (10 c.c.) was added bromine (0.6 g.) in glacial acetic acid (2 c.c.). The reaction mixture was allowed to stand overnight. The oil which separated on addition of water was taken up, washed and dried in ether and after removal of the solvent distilled *in vacuo*. The product, b.p. 232-233°/15 mm., was recrystallised from alcohol and obtained in colourless plates melting at 64°.

(c) 4'-Amino-5-bromo-2-methoxydiphenyl ether (VIII) (Buchan and Scarborough, *loc. cit.*) (4 g.) was converted to its hydrobromide by heating with hydrobromic acid (30% ; 35 c.c.). The suspension was cooled to 0°, sodium nitrite (0.94 g.) slowly added with stirring, the diazotised solution allowed to stand for half an hour, and then poured into hydrobromic acid containing active copper powder. The reaction mixture was allowed to stand for half an hour, then heated on a water bath till the evolution of nitrogen ceased. The product was taken up, washed and dried in ether, and after removal of the solvent was distilled *in vacuo*. It came over at 232-234°/15 mm., and after recrystallisation from alcohol was obtained in colourless plates melting at 64°. The yield was poor.

All these three products melted at 64° alone or admixed with one another or with the product, m.p. 64°, isolated from the monobromination of 2-methoxydiphenyl ether (I).

Found : Br=44.7% ; calculated for C₁₃H₁₀O₂Br₂, Br=44.7%.

4-Bromo-5-Acetamino-2-Methoxydiphenyl Ether (XII).

To a solution of 5-acetylamino-2-methoxydiphenyl ether (Lions and Willison, *loc. cit.*) (2.5 g.) in glacial acetic acid (20 c.c.) was added a solution of bromine (1.6 g.) in glacial

acetic acid (10 c.c.). The colour of the bromine was immediately removed. On standing overnight, white crystals (3.3 g.) were deposited. These were recrystallised from glacial acetic acid and obtained as micro needles melting at 158° (decomp.). This substance was partly hydrolysed by boiling water and ionized bromine formed, as shown by the precipitation of silver bromide on addition of silver nitrate. It fumes in moist air, and its solution attacks filter paper. It is decomposed by heating in most solvents, especially if water or alcoholic groups are present. It gives a blue colouration with potassium iodide starch reagent. It seems therefore to be 5-acetbromamino-2-methoxydiphenyl ether (XI), but the percentage of bromine found on analysis—viz. 29.8%—is much higher than that calculated for $C_{15}H_{14}O_3NBr$. The substance may possibly be a partial hydrobromide, and it is noteworthy that the melting point is variable, 158° being the highest value obtained.

This substance may be readily converted to 4-bromo-5-acetylamino-2-methoxydiphenyl ether (XII) by treatment with aqueous or hydroxylic solvents. When its solution in acetone is treated with water, 4-bromo-5-acetylamino-2-methoxydiphenyl ether (XII) is obtained in glistening white plates which may be recrystallised from petroleum ether in white prismatic needles melting at 100° .

This substance does not give hydrobromic acid on heating with water. It has an extremely bitter taste.

Found: Br=23.7%; calculated for $C_{15}H_{14}O_3NBr$, Br=23.8%.

4-Bromo-5-Amino-2-Methoxydiphenyl Ether (XIII).

4-Bromo-5-acetylamino-2-methoxydiphenyl ether (XII) (2 g.) was hydrolysed by refluxing for three hours with a 15% solution of potassium hydroxide in methyl alcohol (30 c.c.). The excess potassium hydroxide was neutralised with carbon dioxide, the precipitated bicarbonate filtered off, and the filtrate diluted with water, when the amine was obtained in prismatic needles which melted at 68° after several further recrystallisations from aqueous methanol.

Found: N=4.6, Br=27.3%; calculated for $C_{13}H_{12}O_2NBr$, N=4.8, Br=27.2%.

4 : 5-Dibromo-2-Methoxydiphenyl Ether (IX).

Treatment of 4-bromo-5-amino-2-methoxydiphenyl ether (XIII) (2 g.) with hydrobromic acid (30% ; 30 c.c.) precipitated the white hydrobromide. This was immersed in an ice bath and diazotised by the addition of sodium nitrite. The diazotised amine was then poured into a cold suspension of finely divided copper in hydrobromic acid (30%), when nitrogen was evolved. The reaction was completed by warming, and the mixture extracted with ether. The ethereal extract was washed with alkali and water, dried and the solvent removed, and the residual oil distilled *in vacuo*. It came over at 230-232°/15 mm. as a colourless oil which solidified on cooling ; and after recrystallisation from ethyl alcohol was obtained in colourless rectangular blocks melting at 83°.

Found : C=43·2, H=2·9, Br=44·4% ; calculated for $C_{13}H_{10}O_2Br_2$, C=43·6, H=2·8, Br=44·7%.

4 : 4'-Dinitro-5-Bromo-2-Methoxydiphenyl Ether (XX).

(a) To 5-bromo-2-methoxydiphenyl ether (II) in a mixture of glacial acetic acid (5 c.c.) and acetic anhydride (5 c.c.) was added a solution of fuming nitric acid ($d=1\cdot5$; 2 c.c.) in glacial acetic acid (8 c.c.). After a few minutes crystals commenced to separate. After about half an hour the crystalline product (2·3 g. ; 100% yield) was collected and recrystallised several times from glacial acetic acid (or alcohol), being obtained in pale yellow micro needles melting at 170°.

(b) To 5-bromo-2-methoxydiphenyl ether (II) (1 g.) was added nitric acid ($d=1\cdot42$; 10 c.c.) and the mixture heated gently until brown fumes just started to be evolved. On allowing to stand, clouds of nitrogen peroxide were evolved and a yellow solid separated. This was filtered off and recrystallised several times from glacial acetic acid (or alcohol) and was obtained in pale yellow micro needles melting at 170°, identical with the above.

(c) To 4'-nitro-5-bromo-2-methoxydiphenyl ether (XXI) (Buchan and Scarborough, *loc. cit.*) (2 g.) in glacial acetic acid (5 c.c.) and acetic anhydride (5 c.c.) was added fuming nitric acid ($d=1\cdot5$; 1 c.c.) in glacial acetic acid (5 c.c.). The nitration product separated after a few minutes and was filtered off, washed and recrystallised several times from glacial acetic acid (or alcohol) and obtained as pale yellow micro needles melting at 170°, identical with the above described products.

Found: Br=21.7%; calculated for $C_{13}H_9O_6N_2Br$, Br=21.7%.

4 : 4'-Dinitro-5-bromo-2-methoxydiphenyl ether (XX) reacts readily with piperidine or morpholine showing the presence of an activated halogen atom or aryloxy group or both.

5-Morpholyl-4 : 4'-Dinitro-2-Methoxydiphenyl Ether (XXII).

4 : 4'-Dinitro-5-bromo-2-methoxydiphenyl ether (XX) (1 g.) was heated with morpholine (2 c.c.) in a boiling water bath for two hours. On cooling the reaction mixture set to a gel. To this was added dilute hydrochloric acid, and the gummy mass procured was dissolved in alcohol, from which on cooling (XXII) separated as bright orange acicular needles which melted at 191° after several recrystallisations.

Found: N=11.0%; calculated for $C_{17}H_{17}O_7N_3$, N=11.2%.

4'-Bromo-5-Nitro-2-Methoxydiphenyl Ether (XVII).

(a) To 5-nitro-2-methoxydiphenyl ether (XXV) (Lions and Willison, *loc. cit.*) (2.5 g.) in glacial acetic acid (20 c.c.) was added bromine (1.6 g.) in glacial acetic acid (10 c.c.).

After 12 hours, pale yellow prismatic needles had separated. The whole was diluted with water and the solid (3.0 g.; yield 100%) filtered off and well washed. Several recrystallisations from alcohol (or glacial acetic acid) gave glistening, pale yellow needles or leaflets melting at 150° .

(b) To 4'-bromo-2-methoxydiphenyl ether (VI) (1 g.) in glacial acetic acid (7 c.c.) was added nitric acid ($d=1.42$; 1.5 c.c.) in glacial acetic acid (3 c.c.) and the mixture kept at $40-50^\circ$ for a few minutes. On cooling pale yellow needles separated, which were recrystallised from alcohol and obtained in leaflets melting at 150° alone or admixed with the above.

This substance apparently does not react with piperidine.

Found: Br=24.6%; calculated for $C_{13}H_{10}O_4NBr$, Br=24.7%.

4-Nitro-2-Methoxydiphenyl Ether (XXIV).

This has now been obtained in crystalline form.

The oil B (Lions and Willison, *loc. cit.*), if dissolved in alcohol and slowly allowed to evaporate over several months, deposits pale yellow needles, m.pt. 69° , and pale

yellow, transparent, hexagonal blocks, m.pt. 59° . These crystals could be readily separated by hand picking. The former were shown to be 5-nitro-2-methoxydiphenyl ether (XXVI) by comparison, and the latter 4-nitro-2-methoxydiphenyl ether (XXV) by reduction to the corresponding amine and comparison with 4-amino-2-methoxydiphenyl ether.

4-Nitro-2-methoxydiphenyl ether (XXIV) may be recrystallised from petroleum ether. Its solution in petroleum ether is seeded and allowed to stand for about 14 days when deposition is practically complete. The hexagonal blocks still melt at 59° .

Found : N = 5.8% ; calculated for $C_{13}H_{11}O_4N$, N = 5.7%.

ACKNOWLEDGMENT.

The authors desire to express their grateful thanks to Miss D. M. Little, B.Sc., for some of the (micro)analyses recorded in this paper.

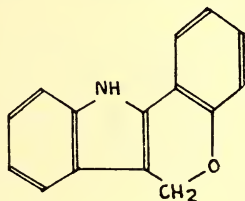
Department of Organic Chemistry,
University of Sydney.

DERIVATIVES OF CHROMANONE.

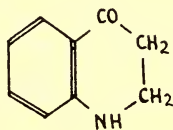
By RITA H. HARRADENCE, M.Sc.,
 GORDON K. HUGHES, B.Sc.,
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(Manuscript received, November 23, 1938. Read, December 7, 1938.)

In continuation of experiments having as their object the formation of indole derivatives by application of Fischer's synthesis (*cf. Journ. and Proc. Roy. Soc. N.S.W.*, 1937, 71, 475-85, 486-493), attempts were made to prepare chromenoindole (I) by cyclisation of the phenylhydrazone of chromanone with various acid reagents.



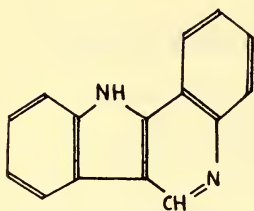
I.



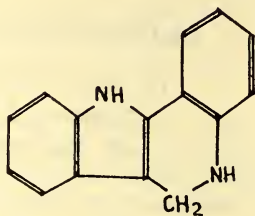
II.

However, it was not found possible to split out ammonia from chromanone phenylhydrazone in this way, and intractable brown oils were the usual product of reaction. Very recently Cawley and Plant (*J.C.S.*, 1938, 1215) reported a similar failure to obtain an indole by the Fischer synthesis from the phenylhydrazone of tetrahydro γ -pyrone—an exactly parallel example. In view of the marked ease of formation of coumaronindoles (*cf. Cornforth, Hughes, Harradence and Lions, Journ. and Proc. Roy. Soc. N.S.W.*, 1937, 71, 486-494; Cawley and Plant, *loc. cit.*) this failure was difficult to understand. However, it will be recalled that Clemo and Perkin (*J.C.S.*, 1924, 1612) were able to show that, whilst an indole could be obtained by cyclisation of the phenylhydrazone of 4-keto-1:2:3:4-tetrahydroquinoline (II), two hydrogen atoms were lost in the process, and that the product was 3:4-

quinindoline with the structure (III) and not the anticipated structure (IV).

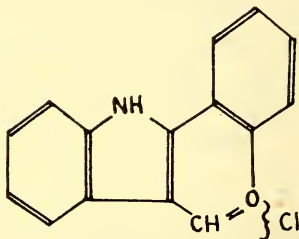


III.



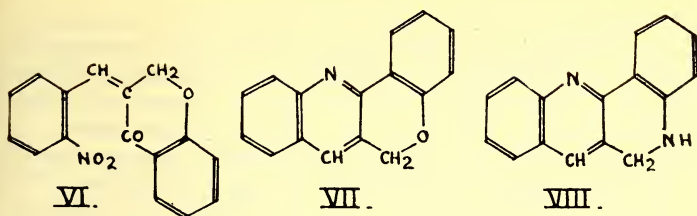
IV.

The loss of two hydrogen atoms in the cyclisation process enables each ring in (III) to attain aromatic character. A similar process could occur with the phenylhydrazone of chromanone only if the oxygen atom were to become 3-covalent, in which case the cyclised product would have to be a pyrylium salt such as (V).



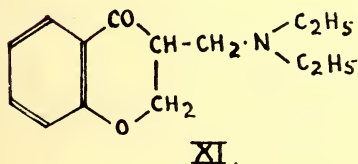
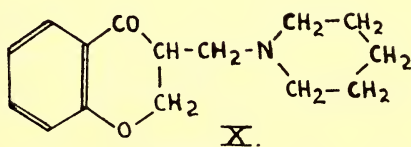
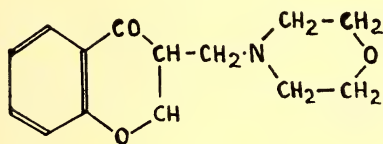
V.

That the failure to effect indole ring closure with the phenylhydrazone of chromanone is not due to any lack of reactivity of the methylene group adjacent to the carbonyl group was shown by the fact that chromanone condenses readily with such aldehydes as *o*-nitrobenzaldehyde, forming 3-*o*-nitrobenzylidene chromanone (VI), which can be reduced to chromeno-(3' : 4' : 2 : 3)-quinoline (VII); a base which can also be prepared directly by an application of Friedländer's synthesis—by condensation of chromanone with *o*-aminobenzaldehyde under alkaline conditions. This chromenoquinoline is, of course, the oxygen analogue of the dihydro-2 : 3-quinolinoquinoline (VIII) prepared by Clemo and Perkin (*J.C.S.*, 1924, 1613).

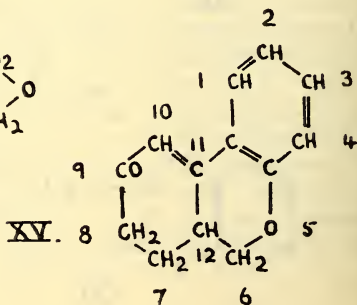
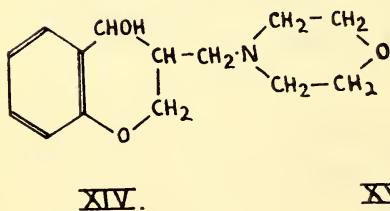
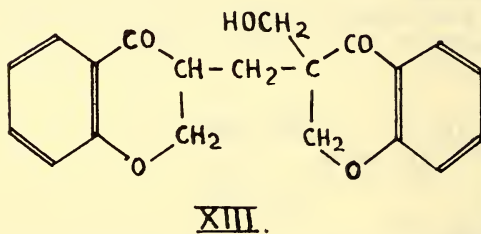
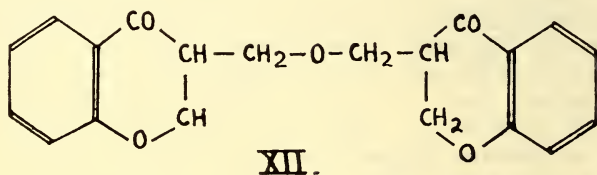


In view of the failure to obtain chromenindole, it was not surprising to find that attempts to eliminate ammonia from chromanone ketazine, and thus to form a dichromenopyrrole, by the method of Perkin and Plant (*J.C.S.*, 1923, 1503) were unsuccessful.

Chromanone was found to behave in the Mannich reaction as a normal ketone containing an active ketomethylene system (*cf.* Mannich, *Arch. Pharm.*, 1917, 255, 261-276; Mannich and Braun, *Berichte*, 1920, 53, 1874; Mannich and Heilner, *ibid.*, 55, 356; Mannich and Lammerung, *ibid.*, 55, 3510, etc.). Thus when chromanone was treated with morpholine hydrochloride and paraformaldehyde in boiling alcohol solution, the hydrochloride of 3-morpholinomethylchromanone (IX) soon crystallised from the reaction mixture. It was similarly possible to prepare 3-piperidinomethylchromanone (X) and 3-diethylaminomethylchromanone (XI).



In the preparation of IX, the formation of a nitrogen-free by-product in small amount was always observed; analysis showed this to have the empirical formula $C_{20}H_{18}O_5$. Attempts to determine its molecular weight ebullioscopically indicated a gradual dissociation on continued boiling, but only the unchanged material could be obtained from the solution on crystallisation. The substance readily formed a dinitrophenylhydrazone, indicating the presence of at least one carbonyl group, but the presence of two such groups could not be established. Without further data we prefer not to assign a structural formula to this substance, but would point out the possibility of its being either (XII) or (XIII), of which structures we are inclined to favour (XIII).



The base (IX) could be readily reduced by Ponndorff's method to 3-morpholinomethylchromanol (XIV), readily characterised by its benzoic and p-nitrobenzoic esters. Of these the former was observed to possess mild local anæsthetic power.

Further, (IX) could be readily induced to form a crystalline methiodide, which was remarkable both for its crystallinity and its stability towards heat. It reacted with sodio acetoacetic ester in alcoholic solution with formation in small yield of 9-keto-12 : 7 : 8 : 9-tetrahydrodibenzopyran (XV). Similar behaviour of Mannich base methiodides has been described by du Feu, McQuillin and Robinson (*J.C.S.*, 1937, 53).

EXPERIMENTAL.

Chromanone Phenylhydrazone (I).

A mixture of chromanone (5.5 g.) and phenylhydrazine (4.0 g.) was warmed at 100° for five minutes. Water commenced to separate almost immediately and the reaction was soon complete. After cooling the yellow oil was separated from the water formed in the reaction and rubbed with petroleum ether, when it soon crystallised. It was recrystallised either from petroleum ether or methanol, coming out from the latter solvent in pale yellow prisms melting at 84°.

Found : N=11.9% ; calculated for $C_{15}H_{14}ON_2$, N=11.8%.

This phenylhydrazone is very unstable, and even when quite pure becomes sticky within 24 hours, and coalesces to a gum.

If dry hydrogen chloride is passed into its alcoholic solution, bright yellow leaflets of *chromanone phenylhydrazone hydrochloride* are precipitated.

Found : N=10.1% ; calculated for $C_{15}H_{15}ON_2Cl$, N=10.2%.

This substance does not melt but decomposes on heating.

All attempts to effect cyclisation of chromanone phenylhydrazone to chromeno-indole proved abortive, such reagents as concentrated hydrochloric acid, alcoholic hydrogen chloride, 10% sulphuric acid, glacial acetic acid, etc., all leading to negative results. The product was usually a dark red-brown oil.

Chromanone Dinitrophenylhydrazone.

Prepared in the usual manner this D.N.P. can be recrystallised from glacial acetic acid, when it comes out in brilliant red prisms melting at 244°.

Found: N=17.2%; calculated for $C_{15}H_{12}O_5N_4$, N=17.1%.

Chromanone Ketazine.

A solution of chromanone (5 g.) in alcohol (40 c.c.) was added to a solution of hydrazine sulphate (4.5 g.) and sodium acetate (7.0 g.) in water (30 c.c.) and the mixture heated under reflux. Crystals commenced to appear within 20 minutes, and after 40 minutes the mass was quite thick and pasty. After cooling, the solid was collected by filtration and recrystallised from alcohol, small bright yellow needles melting at 176° being obtained.

Found: N=9.7%; calculated for $C_{13}H_{16}O_2N_2$, N=9.6%.

Boiling for five minutes with 1:1 hydrochloric acid led to complete hydrolysis of this ketazine and re-formation of chromanone. Attempts to effect its conversion to a pyrrole derivative by the method of Perkin and Plant (*J.C.S.*, 1923, 1503) proved abortive.

3-o-Nitrobenzylidene Chromanone (II).

A solution of chromanone (5 g.) and o-nitrobenzaldehyde (5 g.) in absolute ethyl alcohol (50 c.c.) was saturated with dry hydrogen chloride and then heated at 100° for 30 minutes. It was then cooled, re-saturated with dry hydrogen chloride and again heated at 100° for a further 30 minutes. After cooling, the solid which had precipitated (6.5 g.) was collected and twice recrystallised from ethyl alcohol, being obtained thus in almost colourless needles, which melt at 142°.

Found: N=5.0%; calculated for $C_{16}H_{11}O_4N$, N=5.0%.

Chromeno-(3':4':2:3)-Quinoline (III).

(a) The best method for the preparation of this substance consists of an application of the Friedländer reaction. Sodium hydroxide solution (0.5 c.c. of 20%) was added to a solution of chromanone (3.7 g.) and o-aminobenzaldehyde (3 g.) in absolute alcohol (20 c.c.) and the mixture refluxed on the water-bath for five hours. The

chromenoquinoline (2.5 g.) separated on cooling. After two recrystallisations from alcohol it formed glistening, colourless, minute leaflets melting at 124° .

Found: C=82.0, H=4.7, N=6.0%; calculated for $C_{16}H_{11}ON$, C=82.4, H=4.7, N=6.0%.

(b) Attempts to prepare this same base by reduction of 3-o-nitrobenzylidene chromanone with zinc dust and acetic acid led only to formation of yellow amorphous material. However, when an excess of granulated tin was added to a suspension of II (3 g.) in boiling hydrochloric acid (50 c.c.) reduction and condensation occurred; for after cooling, diluting, and basifying the solution, and then extracting with ether, it was possible to isolate a small amount of crystalline base melting at 119° alone, and at 121° when admixed with the product from (A). It gave a *picrate* melting at the same temperature, viz. 229° , as the base prepared by method (A). The *picrate* crystallises from alcohol in lustrous yellow plates.

Found: N=11.9%; calculated for $C_{22}H_{14}O_8N_4$, N=12.1%.

3-Morpholinomethyl-4-Chromanone.

Chromanone (20 g.), morpholine hydrochloride (13 g.), paraformaldehyde (6 g.) and absolute alcohol (30 c.c.) were refluxed together on the water-bath for 90 minutes. Crystals commenced to separate after the first thirty minutes. After cooling, the hydrochloride of 3-morpholinomethyl-4-chromanone was filtered off and recrystallised from alcohol. It formed colourless plates (15 g.) which melted at $171-172^{\circ}$.

Found: C=59.0, H=6.2, N=5.3%; calculated for $C_{14}H_{18}O_3NCl$, C=59.3, H=6.4, N=4.9%.

The free base was obtained by dissolving the crude hydrochloride in water, and, after removal of a small amount of solid residue (A), basifying the filtered solution with sodium hydroxide solution. It precipitated as a white solid, which was collected and recrystallised from alcohol, from which it came out in rosettes of colourless prismatic needles melting at 93° .

Found: C=67.6, H=6.9; calculated for $C_{14}H_{17}O_3N$, C=68.0, H=6.9%.

The *picrate* was precipitated from an alcoholic solution of the hydrochloride with alcoholic picric acid. Recrystallised from a mixture of alcohol and nitrobenzene it formed bright yellow crystals melting at 172° .

Found : N=11.9% ; calculated for $C_{20}H_{20}O_{10}N_4$,
N=11.8%.

The water-insoluble material (A) mentioned above is a by-product ; it was obtained in considerable amount (13 g.) when a preparation was carried out using chromanone (60 g.) and corresponding quantities of the other reactants. After refluxing this mixture for five hours the alcohol was distilled off and water added. The precipitated heavy oil was taken up in ether. After drying and standing, this solution deposited colourless crystals of the substance (A), insoluble in water and hydrochloric acid, and only sparingly soluble in alcohol. After recrystallisation from alcohol it came out in colourless prisms melting at 167°. It contained no nitrogen or chlorine.

Found : C=71.1, H=5.4% ; calculated for $C_{20}H_{18}O_5$,
C=71.0, H=5.3%.

Treatment of an alcoholic solution of this substance with a solution of dinitrophenylhydrazine in alcoholic sulphuric acid led to separation of a *dinitrophenylhydrazone*, which, after recrystallisation from ethyl acetate, formed a bright red crystalline powder melting at 221°.

Found : N=10.6% ; calculated for $C_{26}H_{22}O_8N_4$,
N=10.8%.

The substance (A) thus contains at least one carbonyl group. Attempts to obtain a bis D.N.P. failed, and the presence of a second carbonyl group could not be proved. Attempts to determine the molecular weight of (A) ebullioscopically led to varying values, the molecular weight apparently diminishing as the boiling proceeded (dissociation), the final reading corresponding to a molecular weight of 177, whereas $C_{20}H_{18}O_5$ requires 338. However, the unchanged material was recovered after removal of the solvent.

3-Morpholinomethyl-4-Chromanol.

A solution of 3-morpholinomethylchromanone (5 g.) and aluminium isopropoxide (4 g.) in absolute isopropyl alcohol (20 c.c.) was kept gently boiling on a water-bath for three hours, whilst the acetone formed in the reaction was distilled off. The solvent was finally distilled off, and after addition of sodium hydroxide solution to the residue, the base was recovered with the help of ether and distilled *in vacuo*. It formed a colourless viscous oil (2 g.) boiling at 175-180°/0.8 mm., which could not be induced to crystallise.

3-Morpholinomethyl-4-Benzoyloxychroman Hydrochloride.

A solution of benzoyl chloride (1 g.) in a little chloroform was gradually added to a solution of the above described alcoholic base (1 g.) in chloroform (5 c.c.) and the mixture allowed to stand overnight. The solvent was then removed and the residue induced to crystallise by rubbing in contact with ether. Recrystallised twice from acetone, it formed colourless needles melting at 177°.

Found: N=3.4%; calculated for $C_{20}H_{24}O_4NCl$, N=3.4%.

3 - Morpholinomethyl - 4 - p - Nitrobenzoyloxychroman Hydrochloride.

Prepared by a method similar to that described for the benzoic ester described above, this substance was obtained in colourless crystals melting at 195° after crystallisation from an acetone-alcohol mixture.

Found: N=6.2%; calculated for $C_{20}H_{23}O_6N_2Cl$, N=6.4%.

3-Morpholinomethyl-4-Chromanone Methiodide.

3-Morpholinomethyl chromanone does not react with methyl iodide in the cold, nor on refluxing with a slight excess of methyl iodide in ethereal solution. Reaction occurs readily in hot alcoholic solution, however, and the product separates in colourless needles melting at 149-150°. The substance may be recrystallised from alcohol, and the unusual stability towards heat of this Mannich base methiodide is worthy of comment.

Found: N=3.7%; calculated for $C_{15}H_{20}O_3NI$, N=3.6%.

Condensation of 3-Morpholinomethyl-4-Chromanone Methiodide with Sodio Acetoacetic Ester.

To a solution in alcohol (50 c.c.) of 3-morpholinomethyl chromanone methiodide [prepared by heating the base (20 g.) with methyl iodide (25 c.c.) under reflux for 30 minutes, and then removing excess methyl iodide *in vacuo*] was added an alcoholic solution of sodio acetoacetic ester [from ethyl acetoacetate (16 g.) sodium (2.8 g.) and absolute alcohol (50 c.c.)] and the mixture refluxed on the water-bath for three hours. It became brown in colour, and sodium iodide precipitated. Most of the solvent was eventually removed *in vacuo*, water added to the residue, and the

separated oil taken up in ether. The ethereal solution was washed with dilute hydrochloric acid twice, then with water, dried, and the solvent removed. The residual oil was fractionated *in vacuo*. After unchanged ethyl acetoacetate had come over, a fraction (5 g.) boiling at 100-110°/1.5 mm. was collected, which proved to be mainly *chromanone*. A second fraction (4 g.) boiling at 205-215°/2.0 mm. was then collected. On cooling this partially solidified, and the solid material was recrystallised from ethyl acetate. It came out in yellow needles melting at 128-130°.

Found: C=77.4, H=6.1%; calculated for $C_{13}H_{12}O_2$, C=78.0, H=6.0%.

The substance is thus, apparently, *9-keto-12:7:8:9-tetrahydrodibenzopyran*.

It readily formed a *dinitrophenylhydrazone*, which was obtained in very deep red needles melting at 250-251° (decomp.) after recrystallisation from a mixture of toluene and alcohol.

Found: N=14.8%; calculated for $C_{19}H_{16}O_5N_4$, N=15.0%.

An attempt to reduce the above described ketone (1 g.) by Clemmensen's method led to formation of an amorphous yellow powdery product which melted indefinitely between 120° and 150°. When shaken with ligroin it imparted a beautiful blue fluorescence to the very dilute solution formed.

3-Diethylaminomethyl-Chromanone Hydrochloride.

Diethylamine hydrochloride (5.6 g.) and paraformaldehyde (4.5 g.) were added to a solution of chromanone (7.4 g.) in alcohol (15 c.c.) and the mixture heated under reflux (water-bath) for two hours. To the cooled solution water and ether were added, and after thorough admixture the aqueous layer was separated, again extracted several times with ether and then allowed to evaporate to dryness *in vacuo*. The crystalline colourless residue was recrystallised from alcohol and obtained in white needles melting at 124°.

Found: Cl=13.0%; calculated for $C_{14}H_{20}O_2NCl$, Cl=13.2%.

3-N-Piperidinomethyl Chromanone.

Piperidine hydrochloride (6.1 g.) and paraformaldehyde (4.5 g.) were added to a solution of chromanone (7.4 g.)

in alcohol (20 c.c.) and the mixture refluxed for three hours. Water was then added to the cooled solution and the whole extracted with ether. The aqueous layer was separated and evaporated to dryness *in vacuo*, a colourless non-crystallisable syrup being obtained. This was taken up in a little water, the solution made alkaline and the liberated base taken up in ether and then finally distilled *in vacuo*. It came over as a yellow viscous oil (3 g.) at 116-117° under a pressure of 1 mm.

Found: C=74.0, H=8.0%; calculated for $C_{15}H_{19}O_2N$, C=73.5, H=7.8%.

ACKNOWLEDGMENT.

The authors gratefully acknowledge their indebtedness to Miss D. M. Little, B.Sc., for several of the (micro)analyses recorded above; whilst the award of a Commonwealth Government Research Scholarship, which has enabled one of them (R.H.H.) to take part in the work, is also gratefully acknowledged.

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THE SYNTHESIS OF DERIVATIVES OF FLUORENE
FROM α -HYDRINDONE VIA THE "MANNICH"
REACTION.

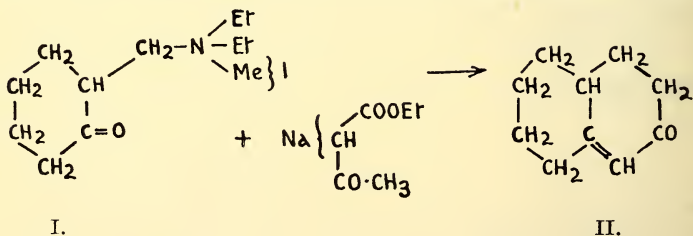
By MISS RITA H. HARRADENCE, M.Sc.,
and FRANCIS LIONS, B.Sc., Ph.D.

(Manuscript received, November 23, 1938. Read, December 7, 1938.)

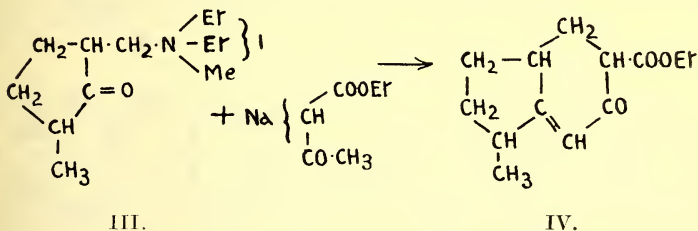
Perhaps the most useful property of the ketonic tertiary bases derived by the Mannich reaction (from ketones containing a ketomethylene system, formaldehyde and a secondary aliphatic base hydrochloride) is the ease with which they lose secondary base to form vinyl ketones. du Feu, McQuillin and Robinson (*J.C.S.*, 1937, 53) seem to have been the first to make use of this property in synthetical work when they employed Mannich bases (as their methiodides) directly as potential sources of $\alpha\beta$ unsaturated ketones which were reacted with reagents of the Michael type—particularly sodio acetoacetic ester.

Thus, as an example (A), 2-diethylaminomethylcyclohexanone methiodide (I) reacted readily with sodio-acetoacetic ester to give a product from which 2-keto- $\Delta^{1:9}$ -octalin (II) was readily isolated; whilst, in another example (B), the methiodide of 2-diethylaminomethyl-5-methylcyclopentanone (III) was reacted with sodio acetoacetic ester to give 5-keto-6-carbethoxy-3-methyl- $\Delta^{4:9}$ -tetrahydrohydrindene (IV).

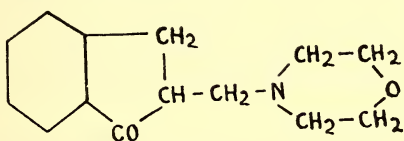
Similar reactions were reported by Mannich, Koch and Borkowsky (*Berichte*, 1937, 70, 355) shortly afterwards, but these authors used the tertiary Mannich bases them-



selves, instead of the methiodides ; and a further extension was that of Reichert and Posemann (*Arch. Pharm.*, 1937, 275, 67), who prepared γ -nitroketones from the interaction of Mannich bases with sodio nitromethane.



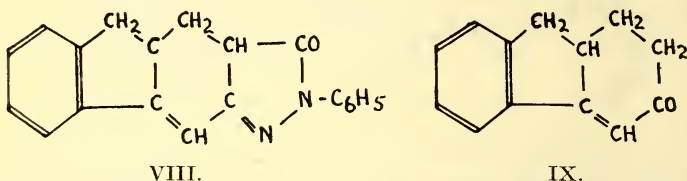
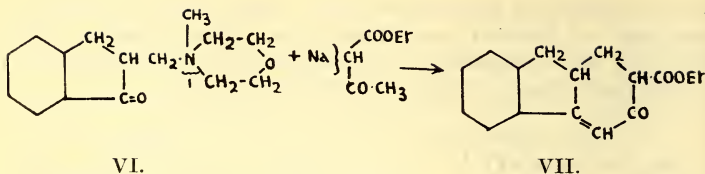
The method elaborated by du Feu, McQuillin and Robinson, and by Mannich, Koch and Borkowsky, in its essentials, is an excellent method for the addition of a fused six carbon ring to any ketone with a reactive keto-methylene system. We now report the results of applying it to the formation of hydrogenated derivatives of fluorene, starting from α -hydrindone. When this ketone is treated with morpholine hydrochloride, paraformaldehyde and alcohol under reflux, reaction soon occurs and the hydrochloride of 2-morpholinomethyl-1-hydrindone (V) is formed in excellent yield, together with a small amount of a basic by-product (C). The base (V) is an uncrystallisable oil which decomposes readily on heating. It reacts easily



V.

with methyl iodide to form the solid methiodide (VI), which, in turn, soon reacts with sodio acetoacetic ester in alcoholic solution to form the sparingly soluble 2-carbethoxy-3-keto-10 : 1 : 2 : 3-tetrahydrofluorene (VII) which separates from the solution in colourless needles.

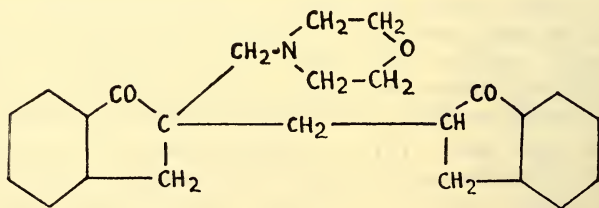
The keto ester (VII) is characterised by its dinitrophenylhydrazone, and its ready formation of the pyrazolone (VIII) when treated with phenylhydrazine in hot alcoholic solution.



Attempts to effect ketone hydrolysis of (VII) with methyl alcoholic potash solutions led to tarry products, but by use of a method due to du Feu, McQuillin and Robinson (*loc. cit.*)—viz. heating to 190° with glycerol containing 10% of water—it was possible to obtain 3-keto-10 : 1 : 2 : 3-tetrahydrofluorene (IX) in moderate yield, as a beautifully crystalline substance, which readily yielded a dinitrophenylhydrazone, and a semicarbazone.

Heat treatment of (IX) at 330° for five hours with palladised charcoal (prepared according to Diels) led to dehydrogenation, and formation of the previously unknown 3-hydroxyfluorene together with some fluorene. Reduction of (IX) with hydrogen and palladised charcoal led to formation of the saturated ketone, 3-keto-1 : 2 : 3 : 4 : 10 : 11-hexahydrofluorene (X)—a colourless oil readily characterised by its dinitrophenylhydrazone and semicarbazone.

The saturated ketone (X) was, in turn, readily reduced by Clemmensen's method to the hexahydrofluorene previously prepared by Cook and Hewett (*J.C.S.*, 1936, 62-71).



X.

Reduction of (IX) with sodium and absolute alcohol gave the saturated alcohol, 3-hydroxy-1 : 2 : 3 : 4 : 10 : 11-hexahydrofluorene, as a colourless oil.

Analyses of the by-product (C) mentioned above, and of its picrate, indicated that such a structure as (X) should be assigned to it.

EXPERIMENTAL.

2-Morpholinomethyl-1-Hydrindone.

A mixture of α -hydrindone (60 g.), morpholine hydrochloride (56 g.), paraformaldehyde (15 g.) and absolute alcohol (90 c.c.) was gently refluxed for two hours. Solution gradually took place, followed by the separation of crystals of the hydrochloride of 2-morpholinomethyl-1-hydrindone after about 30 minutes. The contents of the flask finally set to a solid mass. After cooling the hydrochloride (90 g.) was filtered off. A further 10 grams could be obtained from the filtrate after removal of the alcohol. The crude hydrochloride was dissolved in water, filtered off from a small amount of insoluble material, and extracted with ether to remove any unchanged materials. Evaporation of a portion of this aqueous solution gave the hydrochloride. Recrystallised from alcohol it was obtained in colourless plates melting at 162° .

Found : N = 5.1% ; calculated for $C_{19}H_{18}O_2NCl$, N = 5.2%.

The *picrate*, precipitated from an alcoholic solution of the hydrochloride with alcoholic picric acid, was recrystallised from a mixture of alcohol and nitrobenzene. It formed bright yellow needles melting at 146° .

Found : N = 12.4% ; calculated for $C_{20}H_{20}O_9N_4$, N = 12.2%.

The free base was liberated from the aqueous solution of the hydrochloride with sodium hydroxide. On extraction with ether, a colourless crystalline by-product (C) (about 5 g.) separated, and was removed by filtration. The solvent was removed from the dried ethereal solution by distillation, eventually *in vacuo*. The crude base (51 g.) thus obtained was used as such for condensation experiments. A small amount of the base was distilled in high vacuo and obtained as a colourless viscous oil, boiling over the range $130-152^\circ/3.5$ mm. It could not be induced to crystallise. Considerable decomposition occurred during the distillation and a resinous residue was left in the distilling flask.

The free base reacted with phenylhydrazine in the cold with evolution of heat, but no crystalline product could be isolated.

The by-product (C) was recrystallised from alcohol, in which it was sparingly soluble, forming colourless lustrous plates melting at 143°. The substance is basic, being soluble in hydrochloric acid solution. It possibly has a structure indicated by the formula (X).

Found : C=76.4, H=6.5, N=4.1; calculated for $C_{24}H_{25}O_3N$, C=76.8, H=6.7, N=3.7%.

It gave a picrate, which, when recrystallised from alcohol, formed small yellow crystals melting at 169°.

Found : N=9.3%; calculated for $C_{30}H_{28}O_{10}N_4$, N=9.3%.

2-Carboethoxy-3-keto-10 : 1 : 2 : 3-Tetrahydrofluorene.

2-Morpholinomethyl-1-hydrindone (51 g.) was treated with an excess of methyl iodide (75 g.), warmed for a few minutes on the water-bath, then allowed to stand with occasional shaking at room temperature for 90 minutes, during which time it set to a solid mass of methiodide. Excess methyl iodide was then removed in a vacuum desiccator. To the methiodide (83 g.) was added a solution of sodio acetoacetic ester (prepared from ethyl acetoacetate (45 g.; 1.5 mols.), sodium (7.7 g.; 1.5 mols.) and absolute alcohol (200 c.c.), and the mixture refluxed on the water-bath for three hours. The methiodide rapidly dissolved, and yellow crystals began to separate from the reaction mixture almost immediately. After cooling, the product was filtered off, washed with water to remove sodium iodide, dried, and recrystallised from ethyl acetate (100 c.c.), being thus obtained as colourless glistening needles (22 g.), melting at 157°. It is very sparingly soluble in alcohol.

Found : C=74.9%, H=6.3%; calculated for $C_{16}H_{15}O_3$, C=75.0, H=6.3%.

The dinitrophenylhydrazone was prepared from a solution of the keto ester in a mixture of alcohol and glacial acetic acid with an alcoholic sulphuric acid solution of dinitrophenylhydrazine. It crystallised slowly on standing overnight. Recrystallised from a mixture of alcohol and ethyl acetate it formed bright orange red flat needles melting at 185°.

Found : N=12.8%; calculated for $C_{22}H_{19}O_6N_4$, N=12.8%.

Pyrazolone from (VII) and Phenylhydrazine.

2 - Carboethoxy - 3 - keto - 10 : 1 : 2 : 3 - tetrahydrofluorene (1 g.) and phenylhydrazine (1 g.) were refluxed in alcohol (15 c.c.) on the water-bath for 30 minutes. Solution gradually occurred, followed by precipitation of a colourless crystalline compound. This was insoluble in all organic solvents and was freed from impurities by boiling with a large volume of ethyl acetate and filtering hot. It formed fine, colourless, matted needles, melting at 288°.

Found : N=9.4% ; calculated for $C_{20}H_{16}ON_2$,
N=9.3%.

3-Keto-10 : 1 : 2 : 3-Tetrahydrofluorene.

Attempted hydrolysis of the foregoing ester (VIII) by boiling for eight hours with methyl alcoholic potassium hydroxide yielded only tarry products. More success was obtained using glycerol containing 10% of water at 180-190° (cf. du Feu, McQuillin and Robinson, *J.C.S.*, 1937, 59).

The keto ester (VIII) (22 g.) was refluxed with glycerol (250 c.c.) and water (25 c.c.) for four hours at 180-190°. Solution gradually occurred and carbon dioxide was evolved. After cooling the solution was diluted with twice its volume of water and extracted thoroughly with ether. The viscous oil remaining after removal of the ether was distilled *in vacuo*, giving a product (10 g.) boiling over the range 150-173° (mainly 170-173°) at 2 mm. This crystallised on cooling, and on recrystallisation from a small volume of ethyl acetate gave beautiful, large, colourless prisms, m.p. 100°. It is readily soluble in alcohol and benzene and insoluble in petroleum ether.

Found : C=82.8, H=6.8% ; calculated for $C_{13}H_{12}O$,
C=84.8, H=6.5%.

The dinitrophenylhydrazone, prepared in the usual manner, was recrystallised from xylene, forming beautiful, deep red, glistening needles, m.p. 248°.

Found : N=15.7% ; calculated for $C_{19}H_{16}O_4N_4$,
N=15.4%.

The semicarbazone, prepared in cold aqueous alcoholic solution in the presence of sodium acetate, was recrystallised from dioxane or aqueous acetic acid forming small colourless crystals melting at 234°.

Found : N=17.5% ; calculated for $C_{14}H_{15}ON_3$,
N=17.4%.

3-Keto-1 : 2 : 3 : 4 : 10 : 11-Hexahydrofluorene.

3-Ketotetrahydrofluorene (1 g.) was hydrogenated at room temperature and atmospheric pressure in the presence of palladised charcoal (prepared from palladium chloride (0.1 g.) and norite (0.5 g.)). The product was obtained as a colourless oil boiling at 142-144°/1.3 mm.

Found : C=81.3, H=7.3%; calculated for $C_{13}H_{14}O$, C=83.9, H=7.5%.

The dinitrophenylhydrazone, recrystallised from a mixture of benzene and alcohol formed flat orange-red plates, m.p. 215°.

Found : N=15.7%; calculated for $C_{19}H_{18}O_4N_4$, N=15.3%.

The semicarbazone, recrystallised from alcohol formed colourless needles melting at 220°.

Found : N=16.1%; calculated for $C_{14}H_{17}ON_3$, N=17.3%.

3-Hydroxy-1 : 2 : 3 : 4 : 10 : 11-Hexahydrofluorene.

3-Keto-10 : 1 : 2 : 3-tetrahydrofluorene (1 g.) was reduced in alcoholic solution (30 c.c.) by means of sodium (3 g.), a little water being added finally to complete the solution of the metal. The solution was acidified with concentrated hydrochloric acid, filtered from precipitated sodium chloride and the alcohol removed by distillation. The residue was diluted with water, the insoluble oil extracted with ether and the ethereal solution dried over anhydrous sodium sulphate. After removal of the ether the product distilled at 135-140°/1.2 mm. Attempts to prepare a crystalline acetate, p-nitrobenzoate, and phenyl urethane failed, possibly due to the fact that the product consists of a mixture of stereoisomers.

Found : C=81.1, H=8.4%; calculated for $C_{13}H_{16}O$, C=83.0, H=8.5%.

3-Hydroxyfluorene.

3-Keto-10 : 1 : 2 : 3-tetrahydrofluorene (1 g.) was heated at 330-335° for five hours with palladised charcoal, prepared according to Diels (*Ber.*, 58, 1232) from palladium chloride (0.04 g.) and norite (0.2 g.). Evolution of hydrogen rapidly took place and colourless crystals sublimed in the condenser. On cooling the reaction mixture was extracted with ether, filtered from charcoal, and the phenolic portion removed from the ether by shaking with sodium hydroxide.

From the ethereal layer a small amount of fluorene was obtained, identified by melting point and mixed melting point with an authentic sample. The phenol was precipitated from the alkaline solution with carbon dioxide, taken up in ether, and, after removal of the ether, sublimed in high vacuo at 200° . It was purified by resublimation at $200^{\circ}/1$ mm., being thus obtained as colourless needles (60 mg.), m.p. 137° .

Found: C=85.3, H=5.7%; calculated for $C_{13}H_{10}O$, C=85.7, H=5.5%.

1 : 2 : 3 : 4 : 10 : 11-Hexahydrofluorene.

3 - Keto - 1 : 2 : 3 : 4 : 10 : 11 - hexahydrofluorene [crude product from catalytic reduction of 3-keto-10 : 1 : 2 : 3-tetrahydrofluorene (5 g.)] was boiled for five hours with amalgamated zinc (15 g.) in concentrated hydrochloric acid (10 c.c.) and water (20 c.c.), water (2.5 c.c.), being added each hour. After steam distillation the product was extracted with ether, dried and distilled. It came over at $136-138^{\circ}/23$ mm. and showed a beautiful fluorescence.

Found: C=89.8, H=8.8%; calculated for $C_{13}H_{16}$, C=90.7, H=9.3%.

2-Morpholinomethyl-5 : 6-dimethoxy- α -Hydrindone.

Dimethoxy α -hydrindone (10 g.), paraform (3 g.), and morpholine hydrochloride (6.4 g.) were refluxed with 15 c.c. absolute alcohol on the water-bath. Before complete solution had occurred the hydrochloride began to separate, and the contents of the flask had completely solidified after fifteen minutes. On cooling it was filtered and recrystallised from a mixture of alcohol and water, forming pale yellow crystals melting at 183° (6 g.).

Found: C=58.8, H=6.5, N=4.5%; calculated for $C_{16}H_{22}O_4NCl$, C=58.6, H=6.7, N=4.3%.

The picrate, recrystallised from a mixture of alcohol and nitrobenzene, formed yellow needles m.p. $185-186^{\circ}$.

Found: N=10.8%; calculated for $C_{22}H_{24}O_{11}N_4$, N=11.1%.

Attempted Preparation of a Mannich Base from β -Hydrindone.

Morpholine hydrochloride (23.3 g.) and paraform (9.5 g.) were heated to refluxing with absolute alcohol (30 c.c.). β -Hydrindone (25 g.) was added in portions during 30

minutes. A gummy solid began to separate before it was all added and gradually increased in bulk until it all went solid. On cooling it was filtered and dried and weighed (43 g.). This product is insoluble in water and alcohol and all organic solvents and does not melt up to 250°. It is evidently a polymerisation product.

ACKNOWLEDGMENTS.

The authors gratefully acknowledge their indebtedness to Miss D. M. Little, B.Sc., for some of the (micro)analyses recorded in this paper. One of them (R.H.H.) also acknowledges the receipt of a Commonwealth Government Research Scholarship which has enabled her to take part in the work.

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APHID VECTORS OF THE VIRUS OF WOODINESS
OR BULLET DISEASE IN PASSION FRUIT
(*PASSIFLORA EDULIS* SIMS).

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(With Plates VI, VII and one text figure.)

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INTRODUCTION.

The records of the N.S.W. Bureau of Statistics and Economics on production of passion fruit in New South Wales indicate a definite decline in the average yield per vine in recent years. The position in respect of the period 1913-1927 was reported in a previous paper⁽⁶⁾ and subsequent production figures are shown in Table I.

TABLE 1.—*Passion Fruit Production in New South Wales.*

Year Ending 30th June.	Vines in Bearing.	Yield in Bushels.	Average Yield per Vine.
1928	168,649	73,230	0·43
1929	215,425	40,211	0·18
1930	203,895	51,051	0·25
1931	203,035	57,595	0·28
1932	243,454	57,226	0·23
1933	256,471	59,558	0·23
1934	289,242	68,050	0·23
1935	209,007	40,144	0·19
1936	155,336	29,832	0·19
1937	174,940	31,550	0·18

Data in respect of vines in bearing refer only to plantations of one acre and upwards, whereas total yield figures include production from smaller areas also. The average yields computed from available records thus are slightly higher than is actually the case but the figures provide a useful index of the position.

On this basis, the average annual yields per vine for each five-year period from 1913 to 1937 are 0.40, 0.46, 0.31, 0.27 and 0.20 bushels respectively, and when it is recalled that individual vines in commercial production in the past have produced annually yields in excess of two bushels, an average of less than one-fifth of a bushel per vine, as in recent years, is indicative of a very low level of production.

Fungous diseases may cause serious losses from time to time but the most important of these diseases, Brown Spot (*Alternaria passifloræ* Simmonds) may be controlled by the application of Bordeaux mixture at appropriate periods, and there can be little doubt that the widespread incidence of the woodiness or bullet disease is mainly responsible for the present unsatisfactory position.

HISTORY AND DISTRIBUTION OF THE DISEASE.

As previously reported,⁽⁶⁾ the disease has long been known to occur in New South Wales; Simmonds⁽¹⁰⁾ records that since 1931 it has assumed serious proportions in Queensland and is now the most important disease of passion vines in that State. The disease is known to occur also in Victoria. Elsewhere there are records of the occurrence of a mosaic or virus disease affecting species of *Passiflora* in England,⁽¹⁾ Sumatra⁽⁸⁾ and South Africa.⁽³⁾ In Kenya⁽⁵⁾ the record is that of the occurrence of the woodiness virus in passion fruit.

Simmonds⁽¹⁰⁾ reported the occurrence of the woodiness virus in *Passiflora alba* in Queensland as determined by mechanical transmission experiments. Mosaic symptoms on *Passiflora alba* and on *P. carulea* as well as on *Tacsonia mollissima* have been noted in N.S.W. Most of the *Passiflora* species introduced for possible plant improvement purposes have also proved susceptible to the woodiness virus disease.

SYMPTOMS.

The main features of the disease include an abnormal thickening and hardening of the tissues of the pericarp of the fruit of *P. edulis*. This was demonstrated⁽⁶⁾ to be due to the development of sclerenchymatous cells which replaced a considerable portion of the parenchymatous tissue on the inner section of the pericarp. In a previous description⁽⁶⁾ of symptoms on the fruit, reference was made also to the presence, on some fruits, of small scabs or eruptions which appeared to have burst through the skin.

It has since been demonstrated by Simmonds⁽⁹⁾ that this feature is a symptom of the scab disease of passion fruit caused by *Cladosporium* sp. Scab infections may occasionally occur in fruits which are also affected with woodiness. The phellogen discussed by Butler,⁽²⁾ (p. 207) refers only to occasional scab lesions present in sections of woody fruit tissue in the slides which he examined.

Fruits on diseased vines are occasionally stippled or blotched and may show small ring-like markings instead of a uniform green or purplish coloration, but it is not known whether such markings are characteristic of the passion fruit woodiness virus under certain environmental conditions or whether they are manifestations of another virus infection.

The foliage of diseased vines is also distinctive, and is briefly described in a previous paper.⁽⁶⁾ Under mild temperature conditions, terminal leaves are markedly down-curved along the axis of the main veins. In some cases the upper surfaces of the tips of the leaves may press against the under surfaces of their petioles or main veins so that the laminæ are curled in cylindrical fashion. Marked clearing of the veins in these young leaves has been observed. Upper leaves just below the youngest leaves are frequently dipped or pointed downwards more strongly than is the case in normal plants.

An upper immature but unfolded leaf on each of a number of inoculated test plants has been noted as apparently normal during recording of results, and at a subsequent examination, less than 8 hours later, has been observed to be markedly down-curved. The progressive development of the leaf curl symptom in three plants after removal from the glasshouse, is illustrated in Pl. VI, figs. A-D.

The leaf curl symptoms are most evident when growth of the terminal leaves occurs at temperatures below 80° F. Under higher temperature conditions there is less curling, but puckering and mosaic mottling are the first manifestations of the presence of infection. In the present series of studies it was noted that frequently after the development of leaf curl symptoms and while temperatures did not exceed 80° F., there was a tendency for the upper leaves to become chlorotic and subsequently to fall from the plant.

Growth was always checked for the time being and, although terminal growth might be resumed, infected

plants were always shorter than the uninfected controls. Secondary symptoms in the nature of yellowish spots or blotches were frequently observed in leaves which were fully formed at the time of inoculation.

It was apparent that, as in the case of so many other virus diseases, development of symptoms was dependent largely on the nature of the environmental conditions under which the plants were growing. It appeared that reactions occurred most readily in vigorously growing plants exposed to relatively high humidities and to temperatures which did not exceed 70-75° F. Masking was again observed when temperatures exceeded 85° F., although disease symptoms again developed in the new growth of such plants when lower temperature conditions were experienced. It was noted, however, that some infected plants continued to produce diseased foliage under conditions which resulted in the masking of symptoms in most other infected plants.

Although the leaf curl symptom is frequently observed in field plantations, the most commonly noted foliage symptom is that of a malformation, stunting and puckering of the leaves as previously described and illustrated.⁽⁶⁾ This development has always followed the leaf curl symptom in mechanical and vector transmission experiments. Less frequently the malformation of leaves took the form of a reduced development of the lamina. Such leaves were proportionately longer and narrower than normal juvenile leaves or on occasion showed a type of "fern leaf" formation somewhat resembling the type of leaf growth observed occasionally in tomatoes affected with tobacco mosaic (Pl. VII, fig. 1).

It cannot yet be stated whether the various symptoms observed on the virus-infected passion plants result from the action of one or more plant viruses. Assuming that one virus only is concerned it may be indicated at this stage, however, that although complete host range studies of the passion fruit woodiness virus have not been completed, it was not found possible to transmit this virus mechanically to certain Solanaceous plants (*Datura stramonium*, *Lycopersicum esculentum*, *Nicotiana tabacum*, and *Nicotiana glutinosa*) under conditions which permitted ready expression of the common tobacco mosaic virus disease symptoms in such plants.

In the field, the development of woody fruits is recorded only on passion vines showing some of the abovementioned

foliage abnormalities. On completion of the 1928 experiments on mechanical transmission of the disease as previously recorded,⁽⁶⁾ three healthy and three diseased plants were retained under insect-proof conditions in a glasshouse until flowers and fruits were developed in 1929. The flowers were artificially pollinated and fruits were obtained from all vines under observation. Diseased (woody) fruits developed on the vines which had shown and were still showing evidence of mosaic or virus infected leaves and normal fruits were obtained from the healthy vines.⁽⁷⁾

STUDIES ON INSECT VECTORS.

After demonstration that the virus of woodiness could be transferred by mechanical means it was but natural to suggest that insects may be of importance also in the spread of the disease under field conditions.⁽⁶⁾ It is recalled, however, that such an assumption may not be entirely justified by analogy with other virus diseases. Tobacco mosaic, for instance, although readily transferred mechanically or by means of aphid vectors in a tomato crop, presumably only may be transferred mechanically in tobacco crops. All available evidence suggests most strongly that insect vectors are not of importance in dispersal of tobacco mosaic in tobacco plantations, but the disease may be spread most readily in the crop by other means.

Passion vines are subjected to a good deal of handling under commercial conditions. The vines are trained on to upright stakes before being allowed to run along wires approximately 5 ft. from ground level. Side shoots are removed from time to time until the vines reach the wires, the vines are pruned, growth of adjacent vines eventually overlaps on the wires, wind may cause rubbing and abrasion of runners or shoots, and the vines are disturbed when fruits are picked. A good deal of wounding and abrasion of tissues may occur under normal conditions, and thus there are opportunities for ready transference of the woodiness virus by mechanical means.

Observations over a period of ten years indicate that, although a number of species of insects may feed and breed on passion vines in New South Wales, the populations of the various species observed have usually been so limited that serious injury to the vines has not resulted. In fact, generally in field examinations close search has

been necessary to find any insects at all. Only occasional brief infestations of jassids, thrips, and aphids have been observed.

Insects of the orders *Hemiptera* and *Thysanoptera* which have been found feeding on passion vines include the green vegetable bug, *Nezara viridula*, the passion vine leaf-hopper, *Scolytopa australis*, three species of jassids, including one belonging to the genus *Erythroneura*, the brown olive scale, *Saissetia oleæ*, the soft brown scale, *Coccus hesperidum*, the long-tailed mealy bug, *Pseudococcus adonidum*, the green peach aphid, *Myzus persicæ*, the potato aphid, *Macrosiphum solanifolii*, and five species of thrips, including *Hercinothrips bicinctus* (Bagnall). Of the aphid species mentioned, *Macrosiphum solanifolii* was collected even less frequently than *Myzus persicæ*.

Insects Used in Vector Transmission Experiments.

In a series of feeding experiments in 1936, 1937, and the early part of 1938, five species of thrips and three species of jassids were used, but under the conditions of these experiments negative results only were recorded.

In August, 1938, a further series of experiments were conducted with *Hercinothrips bicinctus*, a gregarious foliage-feeding species of thrips, and negative results were again obtained under conditions in which the aphid vectors, referred to later, transmitted the disease.

In a limited series of experiments later in 1937, there were indications that aphids were capable of transmitting the disease, but conditions at the time of the experiments were not ideal for the expression of symptoms.

Detailed experiments with aphids were commenced in 1938 and four species were used, viz. *Myzus persicæ*, *Macrosiphum solanifolii*, and two dark species belonging to the genus *Aphis*. The latter were obtained from velvet beans (*Stizolobium* sp.) and from cotyledons (*Cotyledon valida*), and resembling one another closely were thought to be one species until critical examination by Mr. E. H. Zeck, Assistant Entomologist of the N.S.W. Department of Agriculture, indicated that the populations on each host were distinct species. Both forms belong to the group in which are included *Aphis rumicis*, *Aphis medicaginis*, etc., in which there is considerable divergence of opinion as to the synonymy of the species concerned.

In Tables 2 and 3, Mr. E. H. Zeck has set out comparisons of certain morphological features of the two species.

TABLE 2.—Essential Morphological Characters* of *Aphis sp. A*† from *Stizolobium sp.*

Alate Forms.				Apterous Forms.					
Specimen No.	Antennal Segments.			No. of Hairs on Cauda.	Length of Cornicles.	No. of Hairs on Cauda.	Length of Cornicles.		
	III.	IV + V.	No. of Sensoria.					Antennal Segments.	
								III.	IV + V.
	Length.	Length.		Length.	Length.				
1	7	10	3-4	4	5	4	9		
2	8	11	3-4	4	5	4	6		
3	7	9	3-4	4	5	4	8		
4	7	9	6-3	4	5	4	8		
5	7	10	3-4	4	6	4	7		
6	8	11	4-5	4	5	4	6		
7	7	10	4-5	4	5	4	5		
8	7	11	3-3	—	5	3	8		
9	8	11	4-3	4	5	4	6		
10	7	10	3-4	4	5	4	6		

* Figures for length indicate micrometer divisions.

† Collected Sydney, N.S.W., Aug., 1938.

TABLE 3.—Essential Morphological Characters* of *Aphis* sp. B† from *Cotyledon* valida.

Specimen No.	Alate Forms.				Apterous Forms.					
	Antennal Segments.			Length of Cornicles.	No. of Hairs on Cauda.	Specimen No.	Antennal Segments.		Length of Cornicles.	No. of Hairs on Cauda.
	III.	IV + V.	Length.				III.	IV + V.		
1	9	5-4	12	5	5	9	13	10	4	
2	10	7-6	14	6	6	—	—	8	6	
3	11	9-6	14	5	5	3	12	8	5	
4	9	7-8	13	6	6	4	10	8	5	
5	11	8-8	16	7	5	5	11	8	4	
6	10	8-9	13	6	6	6	12	8	—	
7	9	9-6	12	6	5	7	12	8	6	
8	9	7-7	13	6	6	8	13	8	6	
9	11	7-6	14	6	6	9	13	9	4	
10	11	10-9	14	7	—	10	12	9	6	

* Figures for length indicate micrometer divisions.

† Collected Sydney, N.S.W., Aug., 1938.

Critical differences between them are also illustrated by him in text-fig. 1. According to his summary also, the two species may be distinguished as follows :

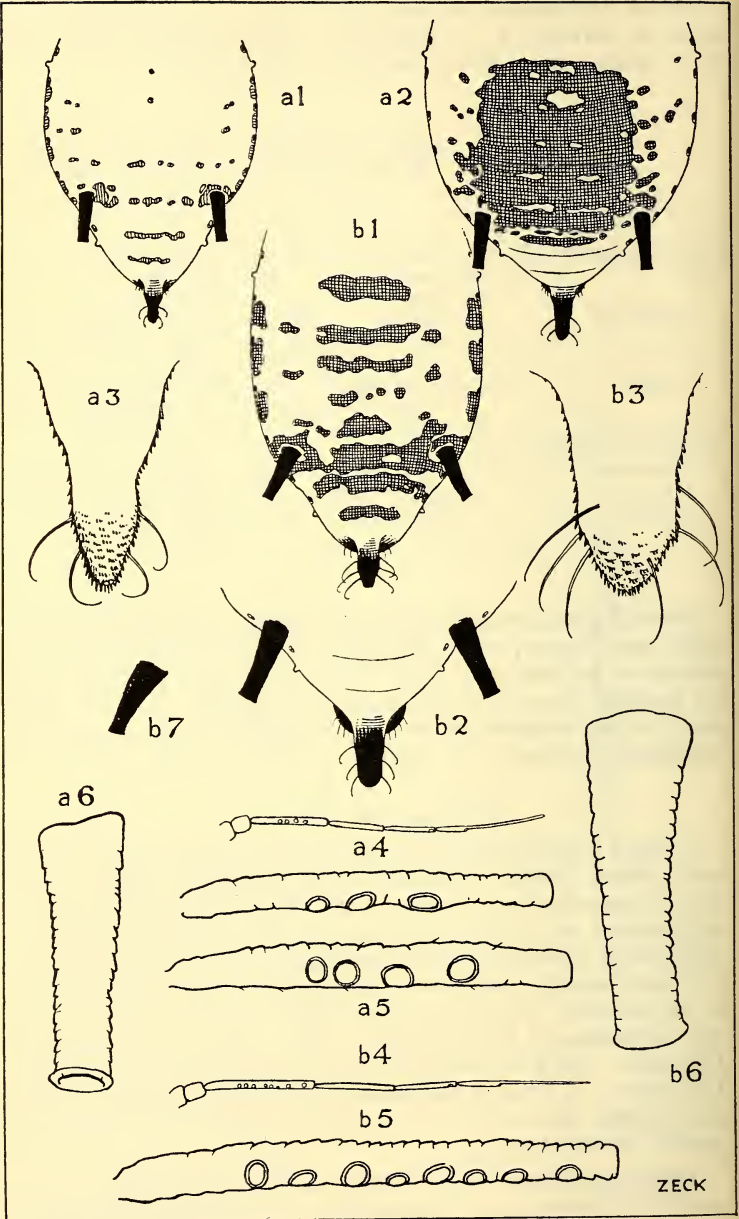
—	<i>Aphis</i> sp. <i>A</i> from <i>Stizolobium</i> sp.	<i>Aphis</i> sp. <i>B</i> from <i>Cotyledon</i> <i>valida</i> .
Alate viviparous ♀♀	With from 3 to 6 sensoria on Antennal III.	With from 4 to 10 sensoria on Antennal III.
Abdomen ..	Without definite central markings.	With definite irregular dark markings.
Cauda	Rather narrow somewhat pointed, with 4 hairs.	Rather broad, rounded at extremity with 5 to 6 hairs.
Apterous viviparous ♀♀		
Abdomen ..	With large dark central mark.	Without central marking.
Cauda	With from 3 to 6 hairs.	With from 4 to 6 hairs.

Both *Myzus persicae* and *Macrosiphum solanifolii* have a wide host range, and, although thus far only these two species of aphids have been observed feeding and breeding on passion vines in the field, both *Aphis* sp. *A* and *Aphis* sp. *B* when transferred to passion vines in the glasshouse continued to feed and breed in a normal manner.

Materials and Methods.

Several thousand passion vines were readily raised from seed either freshly extracted from fruits or after a few days fermentation in water. As the woodiness disease is widespread in N.S.W., it may safely be assumed that apparently normal fruits on the market have been produced on vines which have shown symptoms of the disease, but in no instance during the past three years has there been any evidence of transmission of the disease by means of the seed. All pots and soil were sterilised in an autoclave before use. The seed was sown in the summer of 1937-1938, and plants were from five to nine months old during the period of the tests.

Infected plants were secured in the first instance as a result of mechanical transmission by methods previously



reported.⁽⁶⁾ The aphids were collected from various sources as indicated later. During the feeding process the insects were kept in association with diseased or with healthy plants by means of cellophane sleeves four to five inches in diameter in which the upper portions of the plants were enclosed. The sleeves were prepared from sheets of cellophane, the edges of which were sealed with gold size, thus forming an open cylinder. The sleeves were placed over the plant, tied with raffia at the base round the lower part of the stem, and after insertion of insects were tied at the upper end round a piece of small glass tubing, plugged with cotton wool and supported by a stake. (Pl. VII, fig. 2.)

In tests with single vectors, the latter were enclosed in tubes held in position over portion of the leaf by means of a spring clip and pad in a slight modification of the method devised by Storey.⁽¹²⁾

After removal from original host plants, some insects were enclosed with healthy passion plants and others with virus infected plants. For convenience these were termed healthy "feeder" and diseased "feeder" plants. After varying periods, the insects from each type of plant were transferred to healthy passion plants known as test plants.

In some instances in order to facilitate expression of a virus, if any, carried by the vectors from the original non-passion fruit host plants, the insects were first placed in bulk on apparently healthy plants—known as "pre-feeder" plants—before subsequent transfer to healthy

EXPLANATION TO TEXT-FIGURE 1.

- a1. Abdomen of alate viviparous female. ($\times 45$.)
 - a2. Abdomen of apterous viviparous female. ($\times 45$.)
 - a3. Cauda of alate viviparous female. ($\times 225$.)
 - a4. Antenna of alate viviparous female. ($\times 45$.)
 - a5. Third segments of antenna of alate viviparous female. ($\times 225$.)
 - a6. Cornicle of alate viviparous female. ($\times 225$.)
 - b1. Abdomen of alate viviparous female. ($\times 45$.)
 - b2. Cauda and cornicles of apterous viviparous female. ($\times 45$.)
 - b3. Cauda of alate viviparous female. ($\times 225$.)
 - b4. Antenna of alate viviparous female. ($\times 45$.)
 - b5. Third segment of alate viviparous female. ($\times 225$.)
 - b6. Cornicle of alate viviparous female. ($\times 225$.)
 - b7. Cornicle of apterous viviparous female showing variation of form. ($\times 45$.)
- a. *Aphis* sp. A from *Stizolobium* sp.
 - b. *Aphis* sp. B from *Cotyledon valida*.

feeder and virus-infected feeder plants and thence to the healthy test plants.

On completion of feeding, insects were destroyed by spraying with nicotine sulphate or were removed by means of a brush or by hand. In the case of the latter method, which was utilised in the early tests only, hands were well washed in soapy water before and after treating each plant. Precautions were taken to avoid possible transfer of the disease mechanically during vector removal operations. The glasshouses also were fumigated periodically during the progress of the tests and no evidence was obtained of transfer of the disease to untreated or to check plants during this period.

Transmission Tests with *Aphis* sp. A.

Large numbers of these aphids were transferred from velvet bean plants to a mechanically infected passion vine which had shown first reaction symptoms on 12/7/38. The results of tests with this vector are summarised in Table 4. In one test (Table 4, Experiment 1), after five days' association, during which the aphids were observed to have fed on the foliage of the diseased plant, approximately forty wingless aphids were transferred to each of three healthy plants and were allowed to feed on these plants for four days. In a somewhat similar test (Experiment 1x) the aphids fed for six days on the same reactor and then were allowed to feed on the test plants for six days.

At the conclusion of the feeding period on these test plants, sleeves and aphids were removed. After six to nine days from the time of transfer of the aphids to the healthy test plants, terminal leaf curl reactions characteristic of the passion fruit woodiness disease developed in all six plants.

The reactions noted in these first experiments (1 and 1x) however, could have resulted from introduction of a virus derived from sources other than that of a diseased passion vine. This, however, would seem most improbable in view of the results obtained with further collections of this aphid from the same velvet bean plants and which consistently failed to demonstrate that the aphids on these plants were naturally infected with a virus capable of bringing about an apparent woodiness virus reaction when transferred to normal passion fruit plants.

TABLE 4.—Transmission of Passion Fruit Woodiness Virus by *Dark Aphis* sp. A.

Experiment.	History and Feeding Period. (Days.)	Date of Transfer to Test Plants and Feeding Period. (Days.)	Number and Types of Vector per Plant.	Number of Days after Transfer when Reaction Noted.	Result.*
1	On M reactor of 12/7/38. (5)	18/7/38 (4)	Approx. 40 wingless.	7-9	$\frac{3}{3}$
1x	On M- reactor of 12/7/38. (6)	19/7/38 (6)	Approx. 40 wingless.	6-9	$\frac{3}{3}$
2	On healthy plants. (4)	2/8/38 (2)	Approx. 10 wingless.	Check.	$\frac{0}{6}$
2a	On V- or M- reactor of 26/7/38. (4)	2/8/38 (2)	10 to 20 wingless including few winged.	6	$\frac{1}{6}$
3	On "prefeeder" healthy plants 2 days thence to healthy plants. (1)	1/9/38 (4)	20 winged on each of four plants. 10 winged on each of two plants.	Check.	$\frac{0}{6}$
3a	On "prefeeder" healthy plants 2 days thence to V- reactors of 27/7/38, 8/8/38 or 15/8/38. (1)	1/9/38 (4)	20 to 80 wingless.	7-25	$\frac{6}{10}$
4	On healthy plants. (5)	28/9/38 (33)	Several hundred in bulk.	Check.	$\frac{0}{15}$
4a	On V- reactor of 25/7/38. (5)	28/9/38 (33)	Several hundred in bulk.	12†	$\frac{8}{15}$

M- reactor = mechanically infected passion plant.

V- reactor = diseased plant resulting from vector transmission.
(Date is that of record of first symptoms in reactors.)

* Numerator = number of infected plants.

* Denominator = total number of test plants used.

† First reaction observed.

In Experiment 2, populations of this *Aphis* sp. *A.* were placed on healthy passion plants prior to transference to the healthy test plants. Aphids from the same source were placed (Experiment 2a) also on diseased passion plants which had developed woodiness symptoms as a result of mechanical or insect transmission infections and on which first symptoms were recorded on 26/7/38. One of the six test plants in the infective vector series developed the leaf curl reaction.

In Experiments 3 and 3a the aphid populations were transferred from the velvet beans firstly to normal passion plants (prefeeder plants), portion of this population was then transferred to several healthy passion plants, and another portion to passion plants which had been infected as a result of previous vector transmissions, then in turn populations from the healthy feeder plants were transferred to healthy test plants and aphids from the diseased feeder plants were transferred to a corresponding series of healthy test plants. The prefeeding plants of both series, the feeding plants in Experiment 3 and check test plants all remained healthy, whereas six of the ten plants in the infective vector series developed symptoms of the woodiness virus. This experiment again indicated that the reactions noted in the test plants arose from a virus which had been obtained from diseased passion vines. Temperatures in the glasshouse in early September were rather higher than was considered desirable, and test plants of Experiments 3 and 3a were held in insect-proof cages at lower temperatures prevailing outdoors for six days prior to removal to the glasshouse for final observations. This procedure had the effect in some cases of checking growth of passion vines, and in some instances symptoms were not observed until 25 days after transfer of the aphids to the test plants, whereas, previously, symptoms were noted six to eleven days after transfer of infective vectors.

Experiments 4 and 4a were conducted in muslin-covered insect-proof cages placed outdoors owing to the existence of high temperature day conditions in the glasshouses. This test was of the same general character as the earlier experiments, except that a bulk aphid population was not transferred to healthy passion fruit plants in the first instance. It was conducted for general comparison with a test in which *Macrosiphum solanifolii* was tested as a vector and here again the dark *Aphis* sp. *A.* populations which had previously fed on virus-infected passion vines

were demonstrated to be capable of transmitting the woodiness disease to other passion vines. As in this instance no steps were taken to eliminate the aphid population after a fixed feeding or association period with the test plants, infective aphids may have moved to certain of the test plants some time after the date of their introduction to the cage. The earliest infection was observed twelve days after commencement of the test and diseased plants were recorded at intervals up to the conclusion of the test on 31/10/38. Low night temperatures again temporarily slowed up plant growth and thus also possibly resulted in increasing time required for expression of first symptoms of the disease.

It was notable, also, that practically all of the reacting plants occurred in the northern section of the cage—nearest the source of strongest illumination. It would appear that the vectors, after liberation, were attracted to the plants in this portion of the cage.

It should be noted, also, that, although the passion plants proved to be congenial hosts for all aphid vectors tested, critical observations on actual feeding times were not made. For purposes of convenience, times of association of vector on the various plants are designated in the tabulated results as feeding times.

Transmission Tests with *Aphis* sp. B.

Aphids from *Cotyledon valida* were utilised in a series of transmission experiments the results of which are recorded in Table 5. The methods adopted were similar to those previously utilised except that a bulk population was not transferred in the first instance to a healthy passion plant for prefeeding. It was thought that if the aphids were carrying naturally a virus capable of causing an apparent woodiness reaction in test passion plants, random selection of aphids would most probably result in the development of symptoms in the feeder plants and the test plants of check plant series.

It will be observed from the tabulated results that reactions were obtained only when populations of this aphid had been rendered infective by feeding in the first place on virus-infected passion plants.

Reactions were secured six to eleven days after transfer of the infective aphids to healthy test plants after feeding in the first place on diseased passion plants during an

TABLE 5.—Transmission of Passion Fruit Woodiness Virus by *Dark Aphis* sp. B.

Experiment.	History and Feeding Period. (Days.)	Date of Transfer to Test Plants and Feeding Period. (Days.)	Number and Types of Vector per Plant.	Number of Days after Transfer when Reaction Noted.	Result.*
5	On healthy plants. (4)	8/8/38 (3)	10 winged or 10 wingless.	Check.	$\frac{0}{6}$
5a	On V- reactor of 25/7/38. (4)	8/8/38 (3)	10 winged or 10 wingless.	7-9	$\frac{4}{6}$
6	On healthy plants. (2)	19/8/38 (5)	20 wingless.	Check.	$\frac{0}{6}$
6a	On M- reactor of 19/4/38 or V- reactors of 25/7/38 or 8/8/38. (2)	19/8/38 (5)	Approx. 20 wingless on each of 9 plants. Approx. 100 wingless on each of 2 plants.	7-11	$\frac{9}{11}$
7	On M- reactor of 22/7/38. (4)	23/8/38 (2)	1 wingless.	13-21	$\frac{2}{24}$
7b	On M- reactor of 22/7/38. (4)	23/8/38 (3)	Approx. 100 wingless.	6-8	$\frac{5}{6}$

M- reactor = mechanically infected passion plant.

V- reactor = diseased passion plant resulting from vector transmission.
(Date is that of record of first symptoms in reactors.)

* Numerator = number of diseased plants.

* Denominator = total number of test plants used.

association period with these plants of from two to four days.

Tests with single aphids resulted in the development of woodiness symptoms in two plants of the 24 plants tested. In this small experiment no special significance is to be attributed to an apparent delay in the expression of a definite reaction. In tests with *Myzus persicæ* reported later, reactions were observed to occur within the same general time limits whether single aphids or small populations of aphids were utilised.

Transmission Tests with *Myzus persicæ* Sulz.

During the progress of tests with the dark aphid species, vector transmission experiments were conducted also with *Myzus persicæ*, the green peach aphid. Populations of this aphid were collected from sprouting potatoes. As in the preliminary experiments with the dark aphids, the first tests merely involved transfer of populations of *Myzus persicæ* after the latter had fed for from one to three days on passion plants mechanically infected with the woodiness virus. As indicated in Table 6 (Experiments 8 and 9) reactions were obtained seven to eleven days after transfer of the aphids to test plants.

The subsequent series of tests involved the use of check plants and of prefeeder as well as check plants as in tests with other vectors, and demonstrated that woodiness virus disease symptoms arose only as a result of the use of vectors which became infective after having fed previously on vines affected with woodiness.

Experiments 8 to 12a, 16, 16a, and 17a were conducted with individual plants enclosed in cellophane. Experiments 15 and 15a were bulk tests conducted in insect-proof cages, in which the check population comprised aphids which had fed on healthy passion plants and the reacting series comprised those which had fed on infected passion plants. The cages were held at low temperatures during the feeding period, growth was checked in some plants, and the reaction period ranged from 10 to 21 days.

The vectors freshly collected from potatoes were not carrying a virus which resulted in the development of reaction in healthy passion plants, as in all cases check plants and prefeeder plants remained healthy.

It is of interest to note, also, that in the tests with *Myzus persicæ* the reacting plants used as feeders were frequently those in which leaf curl symptoms had developed

TABLE 6.—Transmission of Passion Fruit Woodiness Virus by Myzus persicae.

Experiment.	History and Feeding Period. (Days.)	Date of Transfer to Test Plants and Feeding Period. (Days.)	Number and Types of Vector per Plant.	Number of Days after Transfer when Reaction Noted.	Result.*
8	On M- reactor of 19/4/38. (1)	26/7/38 (3)	Approx. 30 winged and wingless.	7-9	$\frac{2}{3}$
9	On M- reactors of 19/4/38 and 30/5/38. (3)	28/7/38 (6)	Approx. 40 winged and wingless.	7-11	$\frac{6}{6}$
10	On healthy plants. (2)	28/7/38 (5)	Approx. 12 winged and 100 wingless.	Check.	$\frac{0}{6}$
10a	On M- reactor of 25/7/38. (2)	28/7/38 (5)	Approx. 10 winged and 100 wingless.	7-10	$\frac{2}{6}$
11	On M- reactor of 25/7/38. (4)	29/7/38 (5)	Approx. 50 winged and wingless.	9	$\frac{1}{5}$
12	On healthy plants. (1)	9/8/38 (3)	10 winged on one plant, 20 wingless on each of five others.	Check.	$\frac{0}{6}$
12a	On M- reactor of 8/8/38. (1)	9/8/38 (3)	10 to 20 winged or wingless.	6-9	$\frac{2}{6}$

M- reactor = mechanically infected passion fruit.

V- reactor = diseased plant resulting from vector transmission.

(Date is that of record of first symptoms in reactors.)

* Numerator = number of infected plants.

* Denominator = total number of test plants used.

TABLE 6.—Transmission of Passion Fruit Woodiness Virus by Myzus persicae.—Continued.

Experiment.	History and Feeding Period. (Days.)	Date of Transfer to Test Plants and Feeding Period. (Days.)	Number and Types of Vector per Plant.	Number of Days after Transfer when Reaction Noted.	Result.*
15	On healthy plants. (4)	19/8/38 (5)	Approx. 60 winged and several hundred wingless. (Bulk.)	Check.	$\frac{0}{9}$
15a	On M- reactor of 12/7/38 and V- reactors of 27/7/38 and 8/8/38. (1)	19/8/38 (5)	Approx. 60 winged and several hundred wingless. (Bulk.)	10-21	$\frac{6}{9}$
16	On "prefeeder" healthy plants one day thence to healthy passions. (1)	26/8/38 (3)	7-10 winged.	Check.	$\frac{0}{6}$
16a	On "prefeeder" healthy plants one day thence to M- reactors of 24/6/38 and 19/7/38 and V- reactor of 27/7/38. (1)	26/8/38 (3)	10 winged for each of 6 plants. 50 winged for each of 2 plants.	6-11	$\frac{3}{8}$
17	On "prefeeder" healthy plants one day, thence to V- reactor of 27/7/38. (1)	31/8/38 (1)	1 winged.	7-8	$\frac{3}{25}$
17a	On "prefeeder" healthy plants one day, thence to V- reactor of 27/7/38. (1)	31/8/38 (1)	7 winged.	8	$\frac{1}{1}$

M- reactor = mechanically infected passion fruit.

V- reactor = diseased plant resulting from vector transmission.

(Date is that of record of first symptoms in reactors.)

* Numerator = number of infected plants.

* Denominator = total number of test plants used.

just prior to their use as feeder plants. This was the case also in a number of the experiments in which *Aphis* sp. *A* was tested as a vector. Observations, however, were made in the *Myzus persicae* tests 10a, 11, and 12a on the portions of the reactor plants from which the presumably infective aphids were obtained. It was noted that reactions were subsequently recorded in test plants only when the vectors were secured from the upper leaves of the diseased feeder plants. It would appear that the virus was not present in the symptomless leaves of the freshly diseased feeder plants during the feeding period of these tests.

Tests with single aphids as recorded in Experiment 17 demonstrated that the virus was transferred to three plants of the 25 plants tested. No attempt was made to determine minimum feeding or transmission times as has been demonstrated for this vector in the case of other virus diseases. The experiment indicated, however, that one aphid might secure the virus after feeding for 24 hours or less on a diseased passion plant and that it might transfer the disease to a healthy passion plant after feeding on it for 24 hours or less.

Transmission Tests with *Macrosiphum solanifolii* (Ashm.).

During August and September, 1938, populations of *Macrosiphum solanifolii* became available, and, although glasshouse conditions were becoming unfavourable on account of high day temperatures, it was decided to test this aphid as a possible vector of the passion fruit woodiness virus. Populations of the aphid were collected from sow thistles or milk thistles (*Sonchus oleraceus*), from tomatoes and later from gladioli.

In experiments 18 and 18a as indicated in Table 7, aphid populations were enclosed on healthy passion plants and on passion plants affected with the woodiness disease. After transfer of aphids from diseased to healthy test plants, leaf curl symptoms were subsequently recorded in two of the four test plants used.

In Experiments 19 and 19a bulk populations of aphids after identification were transferred to healthy prefeeder plants, and portions of these populations were then transferred to healthy feeder and to diseased feeder plants before subsequent transfer to the test plants. Three of the five test plants in the infective vector series developed the leaf curl reaction.

TABLE 7.—Transmission of Passion Fruit Woodiness Virus by *Macrosiphum solanifolii*.

Experiment.	History and Feeding Period. (Days.)	Date of Transfer to Test Plants and Feeding Period. (Days.)	Number and Types of Vector per Plant.	Number of Days after Transfer when Reaction Noted.	Result.*
18	On healthy plants. (2)	1/9/38 (4)	10 wingless.	Check.	$\frac{0}{3}$
18a	On M- reactors of 19/4/38 and V- reactor of 4/8/38. (1)	1/9/38 (4)	10 wingless.	7-11	$\frac{2}{4}$
19	On "prefeeder" healthy plants one day, then to healthy plants. (2)	2/9/38 (3)	10-20 wingless.	Check.	$\frac{0}{3}$
19a	On "prefeeder" healthy plants one day, then to M- reactors of 19/4/38 and 24/6/38 and V- reactor of 27/7/38. (2)	2/9/39 (3)	15.	8-10	$\frac{3}{5}$
20	On healthy plants. (4)	26/9/38 (35)	About 100. (Bulk.)	Check.	$\frac{0}{18}$
20a	On V- reactors of 27/7/38 and 2/9/38. (4)	26/9/38 (35)	About 100. (Bulk.)	10†	$\frac{7}{18}$

M- reactor = mechanically infected passion fruit.

V- reactor = diseased plant resulting from vector transmission.
(Date is that of record of first symptoms in reactors.)

* Numerator = number of infected plants.

* Denominator = total number of test plants used.

† First reaction observed.

In Experiments 20 and 20a, the aphids were enclosed in bulk with eighteen test plants in butter-muslin-covered insect-proof cages after having fed in one instance on healthy passion plants and in the other on plants affected with woodiness. In this test, the aphids were not destroyed at the close of a definite feeding or association period. First reactions were observed ten days after transfer of the presumably infective aphids to the test plants and further records of transmission were noted up to 31/10/38 when the experiment was terminated. In this outdoor test, it was noted as in the outdoor test with *Aphis* sp. A, that most of the reacting plants were situated in the northern portion of the cage in the region close to the source of strongest light intensity.

In all cases as before prefeeder and feeder healthy plants as well as the check or control plants remained healthy. Evidence was obtained as recorded in Table 7 to the effect that *Macrosiphum solanifolii* was capable of functioning as a vector of the virus of passion fruit woodiness.

DISCUSSION.

Tests with two species of the genus *Aphis* and with *Myzus persicae* and *Macrosiphum solanifolii* have demonstrated that these aphids are capable of transmitting the passion fruit woodiness virus from affected to healthy passion plants. Experiments with various species of thrips and of jassids during the past three years did not result in transmission, and it would appear that such insects are not capable of transmitting the disease. Further tests, however, are necessary before it can be stated conclusively that certain aphids only are capable of transmitting the disease.

Myzus persicae and *Macrosiphum solanifolii* are recorded as vectors of other plant viruses. It is possible also that the *Aphis* sp. A and B are also known as plant virus vectors under specific designations among the dark coloured forms in the genus *Aphis*. Such designations, however, can be accepted only with reserve. According to Smith,⁽¹¹⁾ (p. 526), *Aphis rumicis* is recorded as a vector of five distinct plant viruses, *Myzus persicae* (*ibid.*, p. 541) as a vector of at least 21 and possibly 23 plant viruses and *Macrosiphum solanifolii* (*ibid.*, p. 533) of ten plant viruses. Figures such as the foregoing are dependent on the characterisation of the viruses under consideration and on the acceptance of a specific determination for an aphid

such as *Aphis rumicis*. There is, however, an absence of specificity in the above-mentioned aphids for transmission of a particular virus.

Furthermore, investigation has shown that in some cases at least, a large number of aphid species may be capable of transmitting a single plant virus. Drake *et al.*⁽⁴⁾ have recorded that the Onion Yellow Dwarf virus may be transferred by 53 species of aphids as well as by several undetermined species. Zaumeyer and Kearns⁽¹⁴⁾ record that at least eleven species of aphids are capable of transmitting the common bean mosaic virus. It is now generally conceded that in such instances the vectors are merely mechanical conveyors of the virus from one plant to another.

It would appear probable that aphid species other than the four recorded in this paper may be capable of transmitting the virus of passion fruit woodiness, but under field conditions in N.S.W. it is possible that *Myzus persicae* is the most important of the insect vectors concerned.

Recommendations for the control of woodiness have stressed the value of sanitation measures, and such measures have been adopted with success by a number of growers. These measures include the planting only of healthy seedlings, removal of young plants showing woodiness symptoms, and finally the complete eradication of diseased plantations before replanting on the same area or in its vicinity.

Watson⁽¹³⁾ has recorded that the adoption of spraying measures for destruction of *Myzus persicae* during the first few weeks of growth of *Hyoscyamus niger* resulted in increased yields of the crop when cultivated as a biennial.

As passion vines in N.S.W. apparently are subject to visitation by aphids only at infrequent intervals, there is justification for the hope that adoption of aphicidal measures at appropriate periods may be economically practicable and may be of material value in increasing yields and in prolonging the productive life of commercial plantations.

Such measures, in any case, appear worthy of adoption in conjunction with sanitation measures for the development of passion fruit seedlings free from the virus of the woodiness disease.

SUMMARY.

1. Statistical information on the production of passion fruit in N.S.W. indicates the existence of a low level of production as well as a decline in the average production per vine in recent years.

2. The woodiness disease is now regarded as the most serious of the diseases affecting passion fruit.

3. Further observations on the development of symptoms are reported.

4. There was no indication of transmission of the disease by means of the seed.

5. Observations particularly during the past three years, indicated that passion vines are not subject, as a rule, to serious infestation by insects. Occasional infestations by species of jassids, thrips, and aphids were recorded. The aphids *Myzus persicae* and *Macrosiphum solanifolii* were recorded from time to time; the latter, however, appeared to occur even less frequently than the former.

6. It was demonstrated that two species of dark aphids characterised in this paper as *Aphis* sp. *A* and *Aphis* sp. *B*, *Myzus persicae* and *Macrosiphum solanifolii* were capable of transmitting the virus of woodiness disease to passion plants. The disease developed as a rule in from six to eleven days after infective aphids had fed on healthy plants under the conditions of the experiments.

7. In a limited series of tests it was demonstrated, in the case of *Aphis* sp. *B* and *Myzus persicae*, that one aphid could obtain the virus by feeding for 24 hours or less on a diseased passion plant and could transmit the disease after feeding on a healthy passion plant for 24 hours or less.

8. Tests failed to demonstrate that insects other than aphids were capable of functioning as vectors of the woodiness virus.

9. It is suggested that the adoption of aphicidal measures at appropriate periods may be economically practicable. Such measures appear to be worthy of adoption at least in beds of seedling plants in conjunction with other measures designed to minimise the incidence of the woodiness disease.

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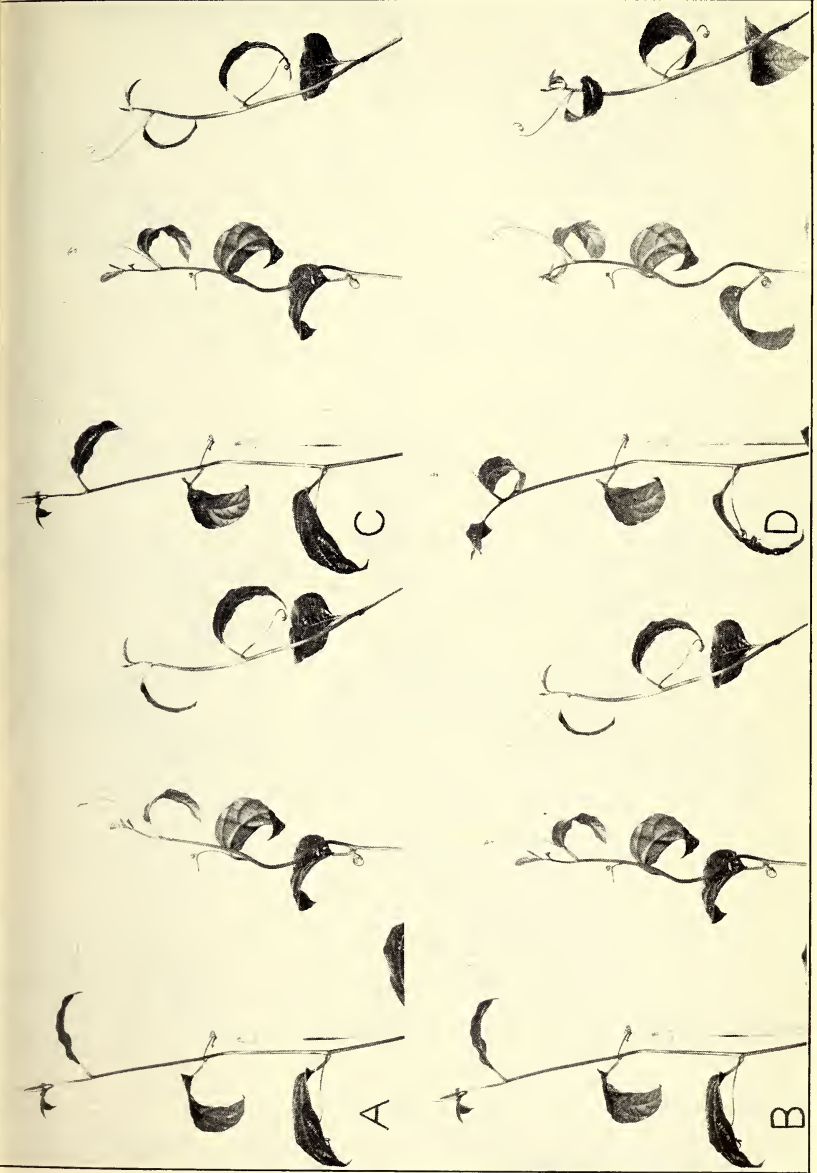




Fig. 2.



Fig. 1.

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EXPLANATION OF PLATES.

PLATE VI.

Passion fruit plants affected with the woodiness virus and showing development of terminal leaf curl symptoms. ($\times \frac{1}{5}$.)

A	photographed	10.30 a.m.	26/8/38.
B	"	12.30 a.m.	26/8/38.
C	"	4.30 p.m.	26/8/38.
D	"	10.00 a.m.	29/8/38.

PLATE VII.

Fig. 1.—Leaves from virus-infected passion fruit plants showing abnormal lamina developments.

Left: Leaf from healthy plant.

Right: Leaves from virus-infected plants. ($\times \frac{1}{5}$.)

Fig. 2.—Passion fruit plant enclosed in cellophane sleeve for insect vector feeding test. ($\times \frac{1}{8}$.)

(Photos by Mr. E. G. Pont.)

NOTE ON SOME SILICIFIED TERRACE SANDS
("GREY BILLY") IN THE HUNTER VALLEY
(N.S.W.).*

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Geological Survey of New South Wales.

(Manuscript received, November 24, 1938. Read, December 7, 1938.)

In 1933 the writer exhibited photographs to the Geological Section of this Society of some boulders of "grey billy" which are to be seen at Abbey Green, three miles south of Singleton, adjacent to the road from Singleton to Jerry's Plains, *via* Warkworth. It was suggested then that the boulders represented remnants of river sands and gravels, the cementation of which had been connected with the outpouring of Tertiary basalt, since removed by denudation. Since that time other outcrops have been discovered which confirm the mode of origin suggested for these deposits.

Following are the salient features of the three principal areas of outcrop of the "grey billy" in the Hunter Valley. Their positions are given in Fig. 1.

1. **Abbey Green**, portions 5 and 44, Parish of Wittingham, County of Northumberland.

Remnants of the deposits cover an area of about 200 acres in these two portions. The surface upon which the boulders rest is extensive, but has been cut into by many small tributaries of the Hunter Valley. Boulders of "grey billy" have been found on this surface for a distance of $2\frac{1}{2}$ miles eastward from the Jerry's Plains road. Most of the boulders have been disturbed during the process of winning gravel for road surfacing. Many of them are upwards of half a ton in weight.

The base of the deposit is at an elevation of 130 feet above the normal water level of the Hunter River.

* Published with the permission of the Under Secretary for Mines, N.S.W.

Fig 1

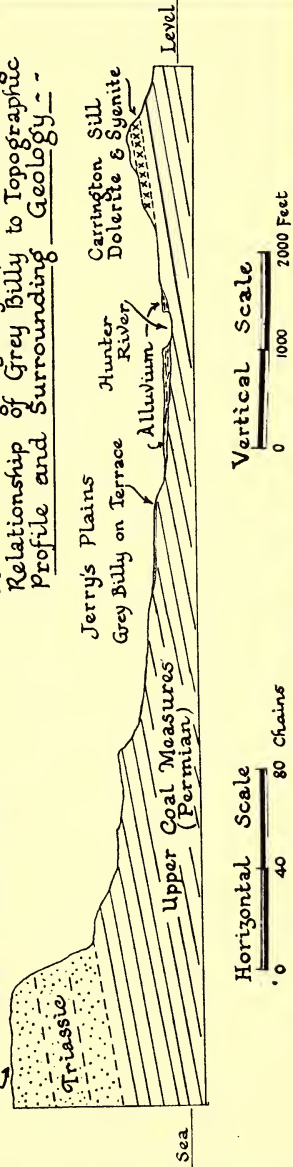
Locality Sketch showing three Principal Areas of Outcrop of Grey Billy in the Hunter Valley . .



Fig 2.

Section through Jerry's Plains showing Relationship of Grey Billy to Topographic Profile and Surrounding Geology . .

Basalt rests on this Surface to South & West



2. Jerry's Plains.

The deposits occur at the western end of the village on the road to Apple Tree Flat and Doyle's Creek. The boulders lie near the edge of a terrace, 130 feet above the level of the Hunter River. The edge of the terrace trends parallel to the river at a distance of 20 chains from it. The boulders have been less disturbed than those at Abbey Green; many of them show approximately flat upper and lower surfaces.

3. Denman Road, 7½ miles from Muswellbrook.

At this locality the country has been denuded of trees, and as the greater part of the deposit remains undisturbed by man, its form can be clearly observed. The "grey billy" forms the edge of a conspicuous terrace adjacent to the Muswellbrook-Denman road at an elevation of about 120 feet above the Hunter River, to which it is parallel and from which it is a mile distant. The terrace has determined the position of the road for at least a mile.

An examination of this occurrence strongly suggests that the blocks of "grey billy" are remnants of a uniform sheet, broken *in situ*, and that they have not been transported to their present position.

The "grey billy" in all of the deposits is closely similar in appearance. The boulders are a pale cream in colour, commonly have an oily lustre, and break with a conchoidal to sub-conchoidal fracture into grey coloured chips. They may be described as hard flinty quartzite. In thin section the rock is seen to be made up of irregular grains of quartz set in a matrix of micro-crystalline siliceous material. The quartz grains are not in contact. The rock is evidently very similar to the "grey billy" of Tallong and the South Coast.⁽¹⁾⁽²⁾

Several reasons may be put forward to prove that the "grey billy" has been formed *in situ*. All the deposits occur as terraces at about the same level. Even if there were no gravel deposits on them, the physiographic evidence clearly proves these terraces to represent an old level of erosion. If the boulders are regarded as transported it has to be explained why no other rock type was carried at the same time.

It has been suggested that the boulders may have rolled from higher ground to their present level, but apart from the fact that the slopes are very gentle for miles adjacent to the first and third of the deposits, there are strong

objections to such an origin, as, for instance, the fact that the boulders occur at the one erosion level many miles apart, and that there is no suggestion of piling such as happens with tumbled debris.

It is common knowledge that sands and gravels can be converted into "grey billy" by the pouring out upon them of lavas, and since it seems beyond question that the deposits have been formed *in situ* it is thought that no other origin can be reasonably suggested for the Hunter River deposits. (It is considered that the fact that the silicified beds are on the one level at widely separated localities rules out the possibility of alteration by sill intrusion.)

Another common feature of "grey billy" deposits is their tendency to break into blocks of more or less uniform size (see ⁽²⁾ for a specific example), commonly four-sided in plan, and it is considered that this fact satisfactorily explains why the Hunter River deposits are characterised by blocks, a large number of which have approximately the same dimensions.

Thus there seems no escaping the fact that the deposits represent the silicified remnants of sand and gravel deposits laid down by an ancestor of the Hunter River and that their silicification was due to basalt lavas which were poured into the old valley.

This conclusion is strongly supported by observations made by other workers in neighbouring areas. J. A. Dulhunty⁽³⁾ has recently discovered basalt *in situ* within the valley of the Goulburn, a tributary of the Hunter River. E. J. Kenny has told the writer of basalt flows in the Binnaway area which can be observed to extend continuously from the tablelands down the valley sides, and W. R. Browne has recorded similar occurrences from the Barigan-Rylstone district.⁽⁵⁾

The section (Fig. 2) shows the relationship of the "grey billy" at Jerry's Plains to the surrounding geology. The Hunter Valley is shown as incised in a peneplain cut out of Mesozoic rocks. (On the north side of the Hunter River the peneplain is cut out of folded Upper Palæozoic rocks.) Basalt rests upon this peneplain in places. In the course of carving out its valley the Hunter River exposed a series of alkaline dolerite and syenite sills, one of which, the Carrington Sill, is shown on the section. Basalt was poured out on the sands and gravels in the bottom of the great valley, converting them in places to "grey billy".

Subsequent uplift of about 130 feet led to renewed stream action, and the removal of the lava and most of the silicified stream deposits.

The alkaline sills referred to have been listed, and one of them described in detail, by H. F. Whitworth and the writer.⁽⁴⁾ They are all of the one family and show many features in common with the intrusive mass at Prospect in the Sydney district and other rocks in New South Wales with teschenitic affinities.⁽⁵⁾

The writer has shown elsewhere that at least one of these sills (Plashett) was intruded during a period of folding.⁽⁶⁾ All of them intrude tilted strata. W. R. Browne⁽⁴⁾ also records tilting associated with the injection of basic intrusives, and J. A. Dulhunty⁽³⁾ has concluded that the intrusion of alkaline dolerites was associated with warping of the Jurassic in the Upper Goulburn Valley.

In the Hunter Valley region, as the section shows, peneplanation post-dates the folding with which the intrusion of the alkaline dolerites is associated.

Peneplanation in turn was followed by uplift of about 2,000 feet. The development of valley-in-valley structure shows that this uplift was episodic. Pouring out of the newer basalts followed. It can be shown that in some places further warping and injection of volcanic necks along tectonic lines accompanied the extrusion of the later flows. As the writer earlier pointed out, there is definite evidence at Murulla (on one of the headwater tributaries of the Hunter) that the injection of basalt necks post-dated the intrusion of the alkaline dolerite sills in this region.⁽⁴⁾

The order of events, therefore, seems to be clearly established but their absolute age can only be determined indirectly. We have, however, two facts which help in spacing these events in geological time. There is clearly a considerable length of time involved in the carving out of great valleys between the two igneous episodes. Just as clearly, erosion since the pouring out of the newer basalts has largely removed evidence of their presence but has only slightly modified the pre-newer basalt topography.

In Victoria, according to F. A. Singleton,⁽⁷⁾ the older basalts are mainly Oligocene in age, being overlain unconformably by Lower Miocene marine deposits. It is, therefore, possible that the alkaline dolerites of East-Central New South Wales may be related to a closing Oligocene orogeny. This view is in substantial agreement with that

of W. R. Browne⁽⁵⁾ and with W. G. Woolnough's⁽⁸⁾ thesis as to the Miocene age of the laterites of the Sydney district.

It may be tentatively concluded that the order of events was :

- (1) Oligocene : Folding and intrusion of alkaline basic sills.
- (2) Miocene : Peneplanation. (Laterites formed.)
- (3) Closing Miocene : Uplift and valley formation.
- (4) Pliocene : Warping, injection of volcanic necks, and pouring out of basalts.

Since the pouring out of the newer basalts the Hunter Valley has experienced an uplift of about 130 feet.

In support of these conclusions, brief reference is made to other areas in New South Wales well known to the author.

In the Condobolin-Lake Cargelligo district, remnants of "grey billy" deposits have been observed on terraces not more than thirty feet above present day tributaries to the Lachlan. The leucite basalts of Lake Cargelligo lie within the broad valley of the Lachlan, and post-date its formation.

In the Trunkey area is a system of plant-bearing leads, capped by basalt, at an elevation of about 3,000 feet. At considerably lower levels and at about fifty feet above the present stream (Grove Creek) are silicified terrace gravels.

It will be seen that it is impossible to maintain (as C. A. Sussmilch has recently attempted to do ⁽⁹⁾) that all the plant-bearing leads are the one age—Lower Pliocene. Moreover, the evidence in the Hunter Valley proves that the pouring out of the newer basalts post-dates the valley formation, which is not of Pleistocene age, but probably Late Miocene to Early Pliocene.

The evidence, therefore, is somewhat at variance with the age usually assigned to the Kosciusko epoch,⁽¹⁰⁾ which is placed as earlier than the newer basalts, and not as post-dating them.

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THE ANTHOCYANIN OF *VITIS HYPOGLAUCA*
F.V.M.

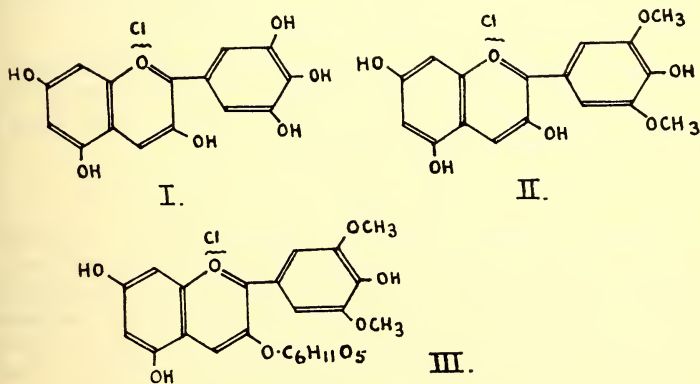
By JOHN W. CORNFORTH, B.Sc.

(Communicated by PROFESSOR J. C. EARL.)

(Manuscript received, November 21, 1938. Read, December 7, 1938.)

Study of grape anthocyanins extending over the past twenty years has shown that these pigments are as a rule monoglucosides of delphinidin (I) or of its methyl ethers.

The cultivated dark-blue grape of Europe, *Vitis vinifera* L., contains oenin (III), with small amounts of other anthocyanins. The anthocyanidin corresponding to oenin is malvidin (II), a delphinidin dimethyl ether. On the other hand, investigation of American grapes by Anderson (*J. Biol. Chem.*, 57, 795; 61, 97; *J.A.C.S.*, 1926, 2997) has shown that three varieties of these grapes, namely *Vitis aestivalis* Michx., *V. labrusca* L., and *V. riparia* Michx., have an anthocyanin which on hydrolysis yields a monomethyl ether of delphinidin, or possibly a mixture of malvidin and delphinidin in equimolecular proportions. Seibel and Isabella grapes, which are hybrids of American and European varieties, contain oenin (III). The wild vine of Europe, *Ampelopsis quinquefolia* Michx. = *V.*



hederacea Ehrh., has an anthocyanin which has been proved by Karrer (*Helv. Chim. Acta*, 10, 67) to be a mixture of malvidin and delphinidin monoglucosides.

It became of interest, therefore, to examine the anthocyanin of an Australian wild grape, in order to see whether the pigment would be oenin, as in the European cultivated grape, or a mixture of glucosides of delphinidin and its methyl ethers, as in the American grape and the European wild vine. To this end a small quantity of the grapes of *Vitis hypoglauca* F.v.M., a wild vine indigenous to Australia, was collected, and the anthocyanin extracted and converted to the picrate. The picrate was recrystallised according to a procedure laid down by Levy, Posternack and Robinson (*J.C.S.*, 1931, 2712) for "natural" oenin picrate. In this way a product was obtained in beautiful slender scarlet needles, which appeared quite homogeneous under the microscope, and which decomposed sharply at 202° (Levy, Posternack and Robinson, *loc. cit.*, give the decomposition point as 202° for synthetic oenin picrate).

The purified picrate was now converted to the chloride. The identity of this chloride with that of oenin (III) was confirmed by "distribution number" determinations as elaborated by Levy and Robinson (*J.C.S.*, 1931, 2720), and also by hydrolysis and identification of the liberated malvidin by the method of Robinson and Robinson (*Biochem. J.*, 25, 1687). The latter method showed that the anthocyanidin contained little or no delphinidin. The distribution number for the anthocyanin chloride was also slightly higher than that given by Levy, Posternack and Robinson (*loc. cit.*) for natural oenin chloride, whereas the presence of less fully methylated delphinidin glucosides would tend to give a lower value.

The anthocyanin of *Vitis hypoglauca* is therefore very largely oenin (III), and resembles in this respect the cultivated grapes of Europe rather than the American grapes or the wild European grape.

EXPERIMENTAL.

Isolation of the Anthocyanin Picrate. 600 g. of *Vitis hypoglauca* grapes were available. The skins were separated, pressed between filter paper, and heated at 90° for a short time to remove external moisture. They then weighed 250 g. The skins were extracted for twelve hours in the cold with 2% methyl-alcoholic hydrogen chloride. The

filtered dark red extract was treated with a large volume of ether, when the crude anthocyanin chloride was thrown down as a dark red syrup. It was taken up in 100 ml. of water and saturated picric acid solution added, both solutions being previously heated to boiling. After cooling the crude picrate was collected, crystallised once from water and then three times from ethyl alcohol and saturated aqueous picric acid after the method of Levy, Posternack and Robinson (*loc. cit.*). The product then formed magnificent scarlet needles decomposing sharply at 202° and appearing perfectly homogeneous and uniform in structure when viewed under the microscope. The tail fractions of the picrate crystallisation yielded dark-coloured irregular crystals. These gave an intense ferric chloride reaction but the amount was too small for further investigation.

The *anthocyanin chloride* was obtained by dissolving the picrate in methyl-alcoholic hydrogen chloride and precipitating with ether. It was crystallised from equal volumes of methyl alcohol and 5N hydrochloric acid. The chloride gave a very weak reaction with ferric chloride in alcoholic solution, a dulling of the brilliant colour and a slight change towards violet being observed. Levy, Posternack and Robinson (*loc. cit.*) record the same result with pure oenin chloride.

The "distribution number" for the chloride between amyl alcohol and 0.5% hydrochloric acid was determined in the usual way. Using a concentration of 1.5 mg./50 ml. the values for two successive shakings were 19.0, 18.8. Levy, Posternack and Robinson (*loc. cit.*) give 17.8 for natural oenin chloride of similar concentration. The close agreement between the values for successive shakings indicates that little or no anthocyanidin is present.

Identification of Anthocyanidin. The chloride (10 mg.) was dissolved in 1% hydrochloric acid and an equal volume of concentrated hydrochloric acid added. After boiling for a short time the solution was cooled and worked up for anthocyanidin as recommended by Robinson and Robinson (*loc. cit.*). The tests described by the same authors were then applied, with the following results:

(i) The amyl alcoholic solution of the anthocyanidin chloride became bluish violet on addition of sodium acetate. When ferric chloride was now added a dulling of the colour was observed, and a faint change towards blue. When ferric chloride was added to the amyl alcoholic

solution without the addition of sodium acetate [Robinson and Robinson (*loc. cit.*); distinction between cyanidin and malvidin] no change was observed.

(ii) On shaking a solution of the substance in 1% HCl with the "cyanidin reagent" only a faint mauve coloration was seen in the upper layer.

(iii) In the "oxidation test" the substance could be recovered with no perceptible loss.

(iv) The anthocyanidin in 1% HCl was completely extracted by shaking out with the "delphinidin reagent".

The behaviour of the substance in these tests corresponds in every way to that of malvidin. Apparently a small amount of impurity gives rise to the weak ferric chloride reaction, but this impurity cannot be delphinidin, which test (iv) shows to be absent.

ACKNOWLEDGMENTS.

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University of Sydney.

THE REACTION OF 3, 5-DINITROBENZOIC ACID WITH ALKALI.

I. THE ISOLATION AND CONSTITUTION OF THE COMPOUND GIVING A RED COLOUR WITH ALKALI.

By ADOLPH BOLLIGER, Ph.D., A.A.C.I.,
and FRITZ REUTER,* Ph.D., A.A.C.I.

(Manuscript received, November 22, 1938. Read, December 7, 1938.)

In 1894, Victor Meyer (*Ber. d. chem. Ges.*, 27, 3151) described the following observations of the reaction which takes place if 3, 5-dinitrobenzoic acid (I) is brought together with solutions of alkali:

(1) An almost colourless solution is resulting if I is just neutralised with alkali hydroxide, or if less alkali is used.

(2) A yellow-red solution is formed if an excess of dilute alkali is added.

(3) A deeply purple coloured solution is formed if a concentrated solution of alkali is added to a solution of I. The colour formed quickly fades, but an intense fuchsin-red colouration appears if this reaction mixture is allowed to stand for more than an hour.

Shukoff (*Ber.*, 1895, 28, 1802) subsequently endeavoured to elucidate these reactions and he reported the isolation of two new substances from solutions of I treated as under (3). One of these substances (II) gave a fuchsin-red solution with dilute alkali and he therefore attributed the colour given by I by the action of strong alkali to the formation of II. Shukoff reports considerable difficulties experienced in trying to prepare appreciable quantities of II, and in some experiments he could obtain only traces of it. He described II as a light yellow amorphous powder which melted unsharply at 200° C. His analytical results agree well with the formula $C_{14}H_{10}N_2O_{11}$ and a molecular weight of 382, and he accordingly assigned to II the constitution of an azoxy-pyrogallie acid. The second substance isolated by Shukoff gave no colour with alkali.

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In connection with the newly developed colour reaction of creatinine with dinitrobenzoic acid in alkaline medium (Bolliger, *THIS JOURNAL*, 1938, 71, 223) it was decided to reinvestigate the problem of the action of alkali on dinitrobenzoic acid. We were able to confirm V. Meyer's observations, and in following Shukoff's technique for the isolation of II we met with the same difficulties.

We succeeded, however, in preparing II in a crystalline state and in a yield of approximately 10% of the I used, when a modified procedure was adopted. The melting point could be raised to 212° C. by recrystallisation, but analytically pure substance melting at 223-224° could be obtained only by sublimation in high vacuum. The analyses are in good agreement with the formula $C_7H_5O_6N$, and determinations of the molecular weight by Rast's method indicate that this formula is correct, and that two benzene nuclei have not been joined as assumed by Shukoff (*l.c.*).

Compound II is a monobasic acid, this accounting for two oxygen atoms, and forms intensely yellow coloured sodium, potassium and ammonium salts. It gives a marked coloration with ferric chloride solutions, indicating the presence of phenolic hydroxyls in the molecule. A deeply red solution is formed if II is dissolved in an excess of alkali, and an unstable tripotassium salt can be isolated from an alcoholic solution, also indicating the presence of phenolic hydroxyls. If an alkaline solution of II is treated with dimethyl sulphate two substances, III and IV, are isolated.

Compound IV analyses for $C_9H_9O_6N$ melts at 138° and gives no colour with ferric chloride. Treatment with strong aqueous alkali converts IV into III, and treatment with methyl alcoholic hydrochloric acid converts III into IV. From this it may be concluded that IV is the methyl ester of III. The melting points and the properties of III and IV are in agreement with those recorded for 3-methoxy-5-nitrosalicylic acid and methyl 3-methoxy-5-nitrosalicylate. (Konek F., *Chem. Z.*, 1930, II, 2892). Furthermore, it is to be expected that under the experimental conditions used, only the hydroxyl in m-position to the carboxyl group would be methylated.

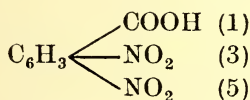
Compound II and IV by the action of stannous chloride in hydrochloric acid solution are converted into amines, both being very readily autoxydised and therefore not isolated in a pure state. This accounts for the two remaining oxygen atoms as being present in a nitro group.

Heating compound II with calcium oxide *in vacuo* effects the removal of the carboxyl group, and 4-nitrocatechol was found to be the main product of this reaction.

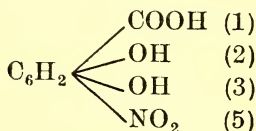
These facts fully support the conclusion that strong caustic alkali acts on 3, 5-dinitrobenzoic acid in such a way as to cause the formation of 2, 3-dihydroxy-5-nitrobenzoic acid, this involving the hydrolytic removal of one nitro group and the introduction of another hydroxyl into the nucleus.

4-nitrocatechol also gives an intense fuchsin-red solution with caustic alkali, similar to that given by II, and approximately the same pH is required to turn the colour of the aqueous solution from yellow to red.

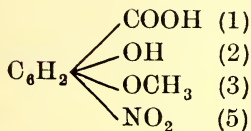
A number of other products are formed in course of the reaction of strong alkali with dinitrobenzoic acid, on which we shall report in another communication.



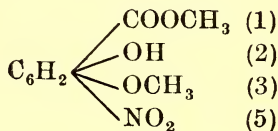
I



II



III



IV

EXPERIMENTAL.

Preparation of Potassium 2, 3-dihydroxy-5-nitrobenzoate.

Numerous experiments were carried out in order to find the conditions for obtaining a maximum yield of II. It was found that light and the presence of traces of heavy metals, such as iron, increase the yield of II. Optimum conditions for preparing II were found to be as follows: 3, 5-dinitrobenzoic acid (10 g.m) is mixed with 12N sodium hydroxide (50 ml.) in an evaporating basin of 30 inches diameter. Complete mixture is brought about by grinding up the suspended acid with a pestle. The mixture takes

on a brownish colour, which deepens on standing towards a deep red. It then is placed under a 75 Watt incandescent lamp and the distance from the globe is adjusted in such a way as to raise the temperature of the reaction mixture to 40° C. While being illuminated and heated the mixture is frequently stirred with the pestle, and soon all the acid has passed into solution, giving rise to the formation of an almost black viscous oil. After five hours the reaction mixture is diluted by the addition of ice and water. Nitrous fumes are given off when the well-cooled solution is acidified by 8N sulphuric acid and the colour of the solution changes to brown, a heavy precipitate being formed at the same time, which is removed by filtration and partly consists of sodium sulphate. The acid filtrate is then continuously extracted with ether, until further extracts give no red colouration with 2N sodium hydroxide.

The light brown coloured ethereal extract is evaporated and the main part of the residual oil crystallises on cooling. This residue is dissolved in the minimum quantity of warm water, cooled to room temperature, and potassium bicarbonate is added in small lots, till the evolution of carbon dioxide ceases. More bicarbonate is then added until yellow needles begin to separate, the yield of which is increased by cooling and the addition of some solid potassium chloride. The crude potassium salt of II is thus obtained in a yield which varies from 7 to 15 per cent. It is further purified by repeated recrystallisation from water. An intense fuchsin-red colour is given by dissolving the salt in aqueous or alcoholic alkali.

Found : K, 13.3 ; N, 4.6%. $C_7H_4O_6NK.3H_2O$ requires K, 13.3 ; N, 4.8%.

Ammonium 2, 3-dihydroxy-5-nitrobenzoate.

This is obtained by treating the aqueous solution of the residue from the ethereal extract with concentrated ammonia, when a deep red solution is obtained. Excess ammonia is removed by evaporation, the colour of the solution turning brown and brownish-yellow needles separating from the concentrated solution. Golden-yellow needles are obtained by repeated recrystallisation from water.

Found, after drying at 20 mm. at 60° C. : C, 38.4, H, 4.1, total N, 12.6 ; ammonia-N, 6.4%. $C_7H_8O_6N_2$ requires C, 38.8, H, 3.7, total N, 12.9 ; ammonia-N, 6.5%.

Preparation of 2, 3-dihydroxy-5-nitro-benzoic acid (II).

This is best obtained from the ammonium salt. The salt (1 gm.) is dissolved in hot N hydrochloric acid (10 ml.). The free acid separates on cooling, still contaminated with some ammonium salt. Light yellow needles are obtained after the crude precipitate has been given another treatment with a few ml. of hot N hydrochloric acid. The melting point was raised to 212° C. by repeated recrystallisations from benzene, and ultimately to 223-224° C. by sublimation (160-170° C. bath temperature at 0.2-0.3 mm. pressure). The sublimate consists of light greenish yellow crystalline aggregates. It is readily soluble in ethyl alcohol, ether, and water, but sparingly soluble in benzene. Its aqueous solution is canary-yellow and the colour is almost completely destroyed by the addition of an acid. It liberates carbon dioxide from an aqueous solution of bicarbonates, giving an intense orange coloured solution and with potassium bicarbonate it forms a sparingly soluble potassium salt.

The solution of II in 0.1 N sodium hydroxide is orange coloured and the colour changes to the typical intense fuchsin-red if the pH is raised to 13.5 or more. The colour with FeCl_3 in aqueous solution is a very intense purplish blue and can be recognised only if using a practically colourless solution of FeCl_3 . It is changed towards a red brown by the addition of a trace of alkali.

Found : C, 41.8 ; H, 3.0 ; N, 7.1%. $\text{C}_7\text{H}_5\text{O}_6\text{N}$ requires C, 42.2 ; H, 2.6 ; N, 7.03%. Molecular weight found, 194, 196 ; required, 199.

Methylation of II. Recrystallised potassium salt of II (3 gm.) was dissolved in 2N sodium hydroxide (20 ml.), giving a deep red solution. Dimethylsulphate (3 ml.) was added in 0.5 ml. lots, the mixture being vigorously shaken and cooled under running water before each addition. The colour changes to an intense orange and a sodium salt begins to separate in yellow needles after the last addition, the separation of which is completed by cooling in ice. An aqueous solution of the yellow sodium salt on acidification with dilute sulphuric acid gave a practically colourless precipitate, m.p. about 90°. It gave a very intense red colour with ferric chloride, and by repeated recrystallisation from water a fraction, m.p. 138°, could be obtained (IV), which gave no colour reaction with ferric chloride.

3-methoxy-5-nitro-salicylic acid (III).

The filtrate from the above sodium salt on acidification with dilute sulphuric acid gave a fawn-coloured precipitate (1.9 g.), m.p. about 190°, which gave an intense red colour with ferric chloride. The m.p. could be raised to 220° by repeated recrystallisation from water, when the substance crystallised in colourless solid needles.

Found: N, 6.53. $C_8H_7O_6N$ requires N, 6.57.

Methyl 3-Methoxy-5-nitro-salicylate (IV).

This was obtained as practically the only product of the methylation when a methylation mixture as in above was heated after the last lot of dimethyl sulphate had been added, and when only a slight excess of alkali was present for the destruction of excess dimethyl sulphate, which was effected by heating on a boiling water bath for 30 minutes. It is best purified by repeated recrystallisation from a large volume of water, from which it separates in long colourless glistening needles, m.p. 138-139°.

Found: C, 47.5; H, 4.0; N, 6.4%. $C_9H_9O_6N$ requires C, 47.6; H, 4.0; N, 6.2%. III and IV readily dissolve in bicarbonate giving intensely yellow solutions.

Decarboxylation of II. The ammonium salt of II (1 gm.) is intimately mixed with calcium oxide (5 gm.). A yellow sublimate is obtained on heating the mixture in a distillation flask at 20 mm. and in a bath of 250°. The sublimate is extracted with ether, the yellow ethereal extract on evaporation leaving a crystalline residue. This was repeatedly recrystallised from benzene. It then melted at 172° and the melting point was not depressed by admixture of an authentic specimen of 4-nitro-catechol, m.p. 174°. Both the analytical and synthetical specimens of 4-nitro-catechol gave yellow aqueous solutions. Addition of bicarbonate to these solutions turned the colour to orange and a deep red colour was produced by the addition of alkali.

Found: C, 46.7; H, 3.4; N, 8.8%. $C_6H_5O_4N$ requires C, 46.4; H, 3.3; N, 9.0%.

ACKNOWLEDGMENT.

Acknowledgment is due to Miss Daphne Little, B.Sc., who made some of the microanalyses, and to Mr. Neil Taylor Hinks for technical assistance.

The Gordon Craig Urological Research Laboratory
and Department of Organic Chemistry,
University of Sydney.

ABSTRACT OF PROCEEDINGS
OF THE
Royal Society of New South Wales

May 4, 1938.

The Annual Meeting, being the five hundred and fifty-ninth General Monthly Meeting of the Society, was held in the Hall of Science House, Gloucester and Essex Streets, Sydney, at 7.45 p.m.

Dr. W. L. Waterhouse, President, was in the chair. Forty-eight members and visitors were present. The minutes of the general monthly meeting of April 6th were read and confirmed.

The certificates of four candidates for admission as ordinary members of the Society were read for the first time.

The certificates of two 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 : Dorothy Hill and Francis Patrick Clune.

The following gentlemen were elected officers and members of Council for the coming year :

President :

PROFESSOR J. C. EARL, D.Sc., Ph.D.

Vice-Presidents :

W. L. WATERHOUSE,
M.C., D.Sc.Agr., D.I.C., F.L.S.
EDWIN CHEEL.

R. J. NOBLE, M.Sc., Ph.D.,
B.Sc.Agr.
R. W. CHALLINOR, F.I.C., F.C.S.

Honorary Secretaries :

PROFESSOR A. P. ELKIN,
M.A., Ph.D.

| C. ANDERSON, M.A., D.Sc.

Honorary Treasurer :

A. R. PENFOLD, F.A.C.I., F.C.S.

Members of Council :

E. C. ANDREWS, B.A.
W. R. BROWNE, D.Sc.
PROF. L. A. COTTON, M.A., D.Sc.
PROF. C. E. FAWSITT, D.Sc., Ph.D.
ASSOC.-PROF. H. PRIESTLEY,
M.D., Ch.M.
H. G. RAGGATT, M.Sc.

PROF. O. U. VONWILLER, B.Sc.,
F.Inst.P.
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. Penfold, were adopted.

THE ROYAL SOCIETY OF NEW SOUTH WALES.

BALANCE SHEET AS AT 31st MARCH, 1938.

		LIABILITIES.					
1937.					1938.		
£		£	s.	d.	£	s.	d.
	Trust Funds—						
	Clarke Memorial Fund ..	1,723	17	10			
	Walter Burfitt Prize Fund	663	18	10			
	Liversidge Bequest ..	652	10	1			
2,964					3,040	6	9
3	Subscriptions Paid in Advance				10	10	0
35	Sundry Liabilities				5	10	7
	Provision for Unexpired Pro- portion of Life Member- ship Subscriptions				155	0	0
153					26,569	13	4
26,261	Accumulated Fund						
<u>£29,416</u>					<u>£29,781</u>	<u>0</u>	<u>8</u>

ASSETS.		1938.					
1937.		£	s.	d.	£	s.	d.
	Cash at Bank and on Hand—						
	The Union Bank of Australia Ltd.	518	2	11			
	Commonwealth Savings Bank of Australia	108	10	11			
	Petty Cash	2	14	3			
243					629	8	1
	Commonwealth Bonds and Inscribed Stock—						
	Bonds (Face Value £4,340)	4,291	10	0			
	Stock (Face Value £2,900)	2,947	6	3			
7,239					7,238	16	3
	Science House Management Committee—						
14,590	Payments to date				14,590	0	0
	Sundry Debtors—						
	Subscriptions Unpaid	334	10	0			
	<i>Less Reserve</i>	334	10	0			
0					0	0	0
6,800	Library				6,800	0	0
	Furniture	452	14	3			
	<i>Less Depreciation written off</i>	22	12	9			
					430	1	6
	<i>Add Additions</i>	4	19	6			
453					435	1	0
	Pictures	50	16	6			
	<i>Less Depreciation written off</i>	2	10	10			
50					48	5	8
	Microscopes	22	11	3			
	<i>Less Depreciation written off</i>	1	2	7			
22					21	8	8
	Lantern	19	0	0			
	<i>Less Depreciation written off</i>	0	19	0			
19					18	1	0
<u>£29,416</u>					<u>£29,781</u>	<u>0</u>	<u>8</u>

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, 1938, 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, 21st April, 1938.

(Sgd.) EDWIN CHEEL,
Honorary Treasurer.

**REVENUE ACCOUNT FOR THE YEAR ENDED
31st MARCH, 1938.**

PAYMENTS.

Year ended 31st March, 1937.		Year ended 31st March, 1938.		
£		£	s.	d.
4	To Advertising	2	15	0
38	„ Cleaning	36	15	0
27	„ Depreciation	27	5	2
5	„ Electric Light and Gas ..	4	13	6
22	„ Insurance	13	19	0
99	„ Library Maintenance ..	85	15	5
2	„ Loss on Sale of Typewriter	0	0	0
67	„ Miscellaneous Expenses ..	49	19	7
249	„ Office Salaries and Audit Fees	261	19	2
	„ Office Sundries and			
18	Stationery	33	11	5
66	„ Printing	81	11	1
	„ Printing and Publishing			
282	Journal	195	16	2
1	„ Repairs	3	3	3
54	„ Stamps and Telegrams ..	49	0	0
17	„ Telephone	14	2	3
	„ Annual Dinner—			
73	Expenses £83 3 9			
57	Less Received 45 13 0			
	—————	37	10	9
16	„ Balance, being Net Revenue for the year, transferred to Accumulated Fund		897	16 9
211			343	14 10
<u>£1,178</u>			<u>£1,241</u>	<u>11 7</u>

RECEIPTS.

Year ended 31st March, 1937.			Year ended 31st March, 1938.	
£	£		£	s. d.
549		By Members' Subscriptions ..	487	4 0
275		„ Government Subsidy ..	400	0 0
171		„ Science House Receipts ..	166	15 0
50		<i>Less</i> Rent Paid ..	39	1 0
—	121		—	—
	50	„ Miscellaneous Receipts ..	127	14 0
280		„ Interest Received ..	46	1 3
		<i>Less—</i>		
		Clarke Me-		
		m o r i a l		
		Fund £66 8 0		
		Walter Bur-		
		fitt Prize		
		Fund 25 10 8		
		Liversidge		
		Bequest 25 1 11		
115			117	0 7
—	165		—	—
	18	„ Proportion of Life Members'	161	12 4
		Subscriptions	19	0 0
			—	—
	£1,178		£1,241	11 7

ACCUMULATED FUND ACCOUNT FOR THE YEAR
ENDED 31st MARCH, 1938.

1938—March 31—		£	s.	d.
To	Arrears of Subscriptions, written off	65	4	0
„	Balance Carried Down	26,569	13	4
		£26,634	17	4
1937—March 31—		£	s.	d.
By	Balance from last Account	26,261	9	6
1938—March 31—				
By	Amount transferred from Bad Debts Reserve			
	Account	29	13	0
„	Net Revenue for the year	343	14	10
		£26,634	17	4
1938—March 31—				
By	Balance Brought Down	£26,569	13	4

Mr. Cheel proposed and Mr. Penfold seconded a motion that Mr. C. F. Horley, of Messrs. Horley & Horley, should be reappointed as the Society's auditor for the year 1938-39. This was the only nomination received, and Mr. Horley was declared elected.

The Annual Report of the Council (1937-1938) was read, and on the motion of Professor Elkin, seconded by Mr. A. R. Penfold, was adopted.

REPORT OF THE COUNCIL (RULE XXVI), 1937-38.

(May, 1937, to April, 1938.)

We regret to report that we have lost by death one life member and one ordinary member, namely, C. W. D. Conacher, elected in 1937, and G. R. Cowdery, elected in 1892.

Two honorary members died during the year: Sir David Orme Masson, elected in 1930, and Professor W. Howchin, elected in 1934. By resignation we have lost one member, and the names of seven members have been removed from the roll for non-payment of subscriptions.

Seven ordinary members were elected during the year, one of whom has since died: C. W. D. Conacher (life member), K. J. Baldick, A. J. Birch, J. A. Dulhunty, J. R. English, Rita H. Harradence, G. K. Hughes.

At the present time (April 30th) the membership stands at 271 ordinary members and seven honorary members.

During the Society's year there have been nine general meetings and ten council meetings. The average attendance at general meetings was 35, and at council meetings 14.

Fifty papers were read during the year, as against thirty-eight last year, and in addition short talks were given at some of the meetings. These were:

"Some Active Volcanoes, with special reference to the recent Vulcanicity at Rabaul", by Professor L. A. Cotton.

"The Geological Background of Soil Erosion", by Dr. W. R. Browne.

"The Biological Background of Soil Erosion", by Professor T. G. B. Osborn.

"The Life and Work of Marconi", by Major E. H. Booth.

Exhibits were shown by Mr. D. P. Mellor and Dr. W. L. Waterhouse.

At one meeting a talkie film entitled "Spanning Space", dealing with all phases of Australian wireless development, was shown by courtesy of Amalgamated Wireless (Australia) Limited.

Four Popular Science Lectures were given, as follows:

15th July.—"French Morocco and its Lessons for Australia", by Professor T. G. B. Osborn, D.Sc.

19th August.—"Glimpses of Tree Life in N.S. Wales", by Mr. R. H. Anderson, B.Sc.Agr.

16th September.—"Modern Astronomy and the Changes it has brought about in our Knowledge of the Heavens", by Mr. James Nangle, O.B.E., F.R.A.S.

21st October.—"Genetics and Problems of Human Subsistence", by Dr. J. G. Churchward, B.Sc.Agr., Ph.D.

All were well attended.

The Annual Dinner was held on April 28th, 1938, at Messrs. Farmer and Company's Restaurant Annexe, and fifty-five persons were present.

The Clarke Memorial Lecture was delivered in the Hall at Science House on March 31st, 1938, by Dr. C. T. Madigan of the University of South Australia, the title of the lecture being "The Simpson Desert and its Borders".

The Clarke Memorial Medal for 1938 was awarded to H. C. Richards, D.Sc., Professor of Geology in the University of Queensland.

Science House.—Meetings of the Science House Management Committee have been held regularly during the year. The Royal Society has been represented at these meetings by Messrs. C. A. Sussmilch and A. R. Penfold. Owing to the absence of Mr. Sussmilch and the departure from Sydney of Dr. Booth, Messrs. E. Cheel and M. B. Welch have been appointed as member and substitute member, respectively, in their places. There has been a fall in the profits of Science House during the year, chiefly due to the fact that the Institute of Architects relinquished its rooms on the fifth floor. Room 510 was also vacated last September, but the Standards Association has occupied an additional room since the middle of January, and is contemplating the lease of further rooms. Several enquiries have been recently received which may lead to the letting of other rooms. The Halls have been very much in demand during the year, and the next few months show promise of further improvement in this direction.

The amount of subscriptions due has been further reduced during the past year, an amount of £120 arrears having been collected.

In June, 1937, His Excellency the Lord Wakehurst became a Patron of the Society.

The Library.

The Council reappointed as Honorary Librarians for the year 1937-38 Professor J. C. Earl and Mr. H. Williams, and they, together with the Executive Officers, were elected as the Library Committee.

Joint Committee on Duplication of Periodicals.—On the suggestion of the Linnean Society of N.S.W., a Joint Committee has been formed to deal with the question of library accommodation and the duplication of periodicals received by the Royal Society and the Linnean Society. The Council of the Royal Society appointed as its representatives on this committee Messrs. C. A. Sussmilch and H. Williams, and Dr. Walkom was appointed convener of the committee. One meeting has been held, and lists of publications received by both societies are under consideration.

Purchase of Periodicals.—The amount of £51 ls. 11d. has been expended on periodicals during the year.

Binding.—A number of parts have been bound at a cost of £33 6s. 6d. Thus the total amount expended on the upkeep of the library for the year has been £84 8s. 5d., which is well within the £100 allowed for in the budget.

Sale of Duplicate Books.—Under arrangement with Mr. Tyrrell of Tyrrell's Limited, a number of duplicates have been handed to him for sale. These include a large collection of old University Calendars which appear to be unsaleable. Mr. Tyrrell has been authorised to dispose of them as waste paper.

The Council further decided to dispose of the collection of medical works in the library. No immediate action has, however, been taken in this matter.

Accessions.—For the twelve months ended February 28th, 1938, the number of accessions entered in the catalogue is 3,666, an increase of over 300 as compared with last year. Of these, 186 were back numbers.

A few new names have been added to the exchange list, but this is balanced by the fact that a similar number has been cancelled, and the "Journal and Proceedings" are still sent, as a gift or exchange, to 353 societies and institutions.

Borrowers and Readers.—The number of visitors to the library during the past year has been 95. Fifty readers' tickets were again issued to the Australian Chemical Institute for the amount of £10. Books from the library have been sent by post in response to requests from kindred societies and universities in Canberra, Victoria, Tasmania, Western Australia, and New Zealand, the only stipulation being that these borrowers should pay postage both ways on the books borrowed. All the books so lent have been returned promptly and in good order.

Additional Shelving.—The Council has decided to act on the Library Committee's recommendation to place ten bays of shelving three feet six inches high at the entrance to the library, for the better display of current periodicals.

On behalf of the Council,
W. L. WATERHOUSE,
President.

The following donations were received: 200 parts of periodicals and 16 whole volumes.

The President, Dr. W. L. Waterhouse, delivered his address, entitled "Some Aspects of Problems in Breeding for Rust Resistance in Cereals".

Dr. Waterhouse, the retiring President, then installed Professor J. C. Earl as President for the year 1938-1939, and the latter briefly returned thanks. Dr. Noble expressed the appreciation of the Society to the retiring President for his work and his address, and Dr. Waterhouse returned thanks to Dr. Noble and the members for their appreciation.

June 1, 1938.

The five hundred and sixtieth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Professor J. C. Earl, President, was in the chair. Eighteen members and two visitors were present. The minutes of the preceding meeting were read and confirmed.

Owing to the fact that only 18 members were present, it was not possible (in accordance with Rule VIII) to hold a ballot for the election of the four persons who had been nominated, and the election was deferred until the next monthly meeting.

The following donations were received: 380 parts of periodicals and 57 whole numbers.

It was announced that the following Popular Science Lectures would be delivered during the year :

July 21 : " Whaling ", by Professor W. J. Dakin.*

August 18 : " The Erect Posture : The Fight against Gravity ", by Professor Harvey Sutton.

September 15 : " Animals and Human Health ", by Dudley A. Gill.

October 20 : " Variable Stars ", by the Rev. W. J. O'Leary.

A letter was received from the Acting Under-Secretary, N.S.W., sending fifty copies of a souvenir booklet from the City of Havre, France, to the City of Sydney, on the occasion of the 150th Anniversary Celebrations.

The following paper was read :

" The Structure of Origanene. Part II. Its Identity with α -Thujene ", by A. J. Birch and Professor J. C. Earl.

An exhibit of Diakon Plastics was shown by Mr. A. R. Penfold.

Professor J. C. Earl gave a short talk on his experiences abroad, with particular reference to the international meetings at which he was the representative of the Royal Society.

July 6, 1938.

The five hundred and sixty-first General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Professor J. C. Earl, President, was in the chair. Twenty-five members and seven visitors were present. The minutes of the preceding meeting were read and confirmed.

The President announced the death of Mr. G. B. Vickery, a member since 1892.

The certificates of two candidates for admission as ordinary members of the Society were read for the first time.

The certificates of four 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 : Marion Breckenridge, Edward L. Griffiths, Christian Westmeath Jeffray-Griffith, and Una Annie Frazer Pickard.

The following donations were received : 302 parts of periodicals, and 18 whole volumes.

* On account of the illness of Professor Dakin, on this date a lecture entitled " The Brain of Fossil Man " was delivered by Professor J. L. Shellshear.

The following papers were read :

- “ Determination of Ascorbic Acid in the Presence of Hæmoglobin ”,
by R. Lemberg and J. W. Legge.
- “ The Bilichrysin, a new Type of Bile Pigment ”, by R. Lemberg
and W. H. Lockwood.
- “ The Heavy Mineral Assemblages of the Upper Coal Measures
and the Upper Marine Series of the Kamilaroi System, New
South Wales ”, by Alma G. Culey.

Professor R. D. Watt gave a short talk entitled
“ Gleanings from a hurried visit to Great Britain ”.

August 3, 1938.

The five hundred and sixty-second General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Professor J. C. Earl, President, was in the chair, and twenty-six members and fifteen visitors were present. The minutes of the preceding meeting were read and confirmed.

The certificate of one candidate for admission as an ordinary member of the Society was read for the first time.

The certificates of two 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: Marie Elizabeth Phillips and Thomas Henry Kennedy Sheahan.

The following donations were received: 252 parts of periodicals and 20 whole numbers.

The following papers were read :

- “ Isonotroso- α -Thujene ”, by A. J. Birch, M.Sc.
- “ 1-Nitroso-menthone Oxime and its Decomposition ”, by Pro-
fessor J. C. Earl, D.Sc., Ph.D., D. Johnson, B.Sc., and J. G.
McKean.

A talk was given by Mr. A. S. Le Souef, entitled “ The Relation of Instinct and Thought Power in the Animal World ”, illustrated by a moving picture film of the birth of a young kangaroo.

September 7, 1938.

The five hundred and sixty-third General Monthly Meeting was held in the Hall of Science House at 7.45 p.m.

Professor J. C. Earl, President, was in the chair. Nineteen members and one visitor were present. The minutes of the preceding meeting were read and confirmed.

The President announced the deaths of Mr. H. C. Kent, a member since 1887, and of Mr. P. C. Trebeck, a member since 1879.

The certificates of three candidates for admission as ordinary members of the Society were read for the first time.

The following donations were received: 345 parts of periodicals and 40 whole numbers. In addition Mr. Andrew James Dixon presented to the library a number of books on mining and metallurgy.

The following papers were read:

- "Coordination Compounds with 8-Aminoquinoline as a Chelate Group", by G. J. Burrows, B.Sc., and E. Ritchie, B.Sc.
- "Note on the Preparation of p-Tolyl Stibinic Acid", by G. J. Burrows, B.Sc., and E. Ritchie, B.Sc.
- "Derivatives of Tetric Acid", by F. Reuter, D.Phil., A.A.C.I., and R. B. Welch, B.Sc.

A talk was given by Dr. A. Albert, entitled "The Conquest of Malaria".

October 5, 1938.

The five hundred and sixty-fourth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Professor J. C. Earl, President, was in the chair. Twenty-two members and one visitor were present. The minutes of the preceding meeting were read and confirmed.

The certificates of four candidates for admission as ordinary members were read for the second time. The following gentlemen were duly elected ordinary members of the Society: Adrien Albert, Samuel Warren Carey, Norman Scott Noble, and John Wallis Powell.

The following donations were received: 215 parts of periodicals and 30 whole numbers.

The following papers were read:

- "Graptolites of the Goulburn District. Part I. Some Forms and Localities", by G. F. K. Naylor, M.A., M.Sc.
- "The Stratigraphy of the Northern Territory, with Special Reference to the Jurassic System", by A. H. Voisey, M.Sc.
- "A Contribution to the Geology of the Eastern Macdonnell Ranges (Central Australia)", by A. H. Voisey, M.Sc.

A talk was given by Mr. A. R. Penfold, entitled "Wool Substitutes".

November 2, 1938.

The five hundred and sixty-fifth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Professor J. C. Earl, President, was in the chair. Thirty-two members and four visitors were present. The minutes of the preceding meeting were read and confirmed.

Alteration to Rules.—The President moved that the following alterations be made to the Rules :

That in Rules IV, XIV, XXVI, XXXVIII " April " be substituted for " May ".

That in Rule XVII " 30th day of April " be substituted for " 31st day of May ".

The motion was seconded by Mr. Challinor and carried unanimously.

The following donations were received : 253 parts of periodicals and six whole volumes.

The following papers were read :

" Some Complex Phthalates ", by G. J. Burrows, B.Sc., and E. Ritchie, B.Sc.

" The Torbanites of New South Wales. Part I. The Essential Constituents and their Relations to the Physical Properties ", by J. A. Dulhunty, B.Sc.

" Preliminary Note on the Nature of the Stresses Involved in the Late Palæozoic Diastrophism in New South Wales ", by S. W. Carey, M.Sc., and G. D. Osborne, D.Sc.

An address was delivered by Mr. W. R. Hebblewhite, B.E., M.I.E.Aust., entitled " Standardisation in Modern Life ".

An exhibit was made by Mr. Cheel of twin seedlings of a palm cocas-yate, and of a book entitled " A Gallery of Gum Trees ", by A. W. D'Ombraïn.

December 7, 1938.

The five hundred and sixty-sixth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

Professor J. C. Earl, President, was in the chair. Twenty-eight members and three visitors were present. The minutes of the preceding meeting were read and confirmed.

Motions from the last Meeting.—Professor J. C. Earl moved that certain alterations to the Rules of the Society, as follows, be approved :

Proposed Alterations to Rules :

That in Rules IV, XIV, XXVI and XXXVIII "April" be substituted for "May".

That in Rule XVII "30th day of April" be substituted for "31st day of May".

This was seconded by Mr. Cheel, and carried unanimously.

The Walter Burfitt Prize.—The President announced that the Council had unanimously decided to award the Walter Burfitt Prize for 1938 to Dr. F. M. Burnet, of the Walter and Eliza Hall Institute, Melbourne.

The following donations were received : 251 parts of periodicals and 27 whole volumes.

The following papers were read :

"Aphid Vectors of the Virus of Woodiness or Bullet Disease in Passion Fruit (*Passiflora edulis* Sims)", by R. J. Noble, Ph.D., M.Sc., B.Sc.Agr., and N. S. Noble, D.Sc.Agr., M.Sc., D.I.C.

"A Chemical Examination of the Fruit of *Pittosporum undulatum*", by J. W. Cornforth, B.Sc., and J. C. Earl, D.Sc., Ph.D.

"The Anthocyanin of *Vitis hypoglauca*, F.v.M.", by J. W. Cornforth, B.Sc. (Communicated by Professor J. C. Earl.)

"The Glycoside of *Persoonia salicina* Fruits", by J. W. Cornforth, B.Sc. (Communicated by Professor J. C. Earl.)

"The Reaction of 3, 5-Dinitrobenzoic Acid with Alkali", I.—"The Isolation and Constitution of the Compound giving a Red Colour with Alkali", by A. Bolliger, Ph.D., and F. Reuter, D.Phil., A.A.C.I.

"The Bromination of 2-Methoxydiphenyl Ether", by F. Lions, B.Sc., Ph.D., and A. M. Willison, M.Sc., A.A.C.I.

"The Use of Morpholine for the Production of 'Mannich' Bases", by Miss R. H. Harradence, M.Sc., and F. Lions, B.Sc., Ph.D.

"Derivatives of Chromanone", by Miss R. H. Harradence, M.Sc., G. K. Hughes, B.Sc., and F. Lions, B.Sc., Ph.D.

"The Synthesis of Derivatives of Fluorene from α -Hydrindone via the 'Mannich' Reaction", by Miss R. H. Harradence, M.Sc., and F. Lions, B.Sc., Ph.D.

"The Condensation of Piperonal with some Succinic Acid Derivatives", by J. W. Cornforth, B.Sc., G. K. Hughes, B.Sc., and F. Lions, B.Sc., Ph.D.

"Researches on Indoles"—

Part VII.—"Derivatives of 7-Nitroindole", by G. K. Hughes, B.Sc., F. Lions, B.Sc., Ph.D., and E. Ritchie, B.Sc.

Part VIII.—"3-Hydroxymethyl Indole-2-Carboxylic Acid Lactone", by Miss R. H. Harradence, M.Sc., and F. Lions, B.Sc., Ph.D.

"Note on some silicified terrace sands ('grey billy') in the Hunter Valley (N.S.W.)", by H. G. Raggatt, M.Sc.

ABSTRACT OF PROCEEDINGS
OF THE SECTION OF
GEOLOGY

1938.

Chairman : Dr. A. B. Walkom.

Honorary Secretary : Mr. R. O. Chalmers.

Eight meetings were held during the year, the average attendance being 13 members and 11 visitors.

1938.

April 29.—Address by Professor L. A. Cotton, "Some Notes on the Occurrence of Tin in North-eastern Tasmania".

May 20.—Address by Mr. J. A. Dulhunty, "Some Notes on the Essential Constituents of Certain New South Wales Torbanites".

June 17.—Exhibits : By Dr. Germaine A. Joplin : (a) Plumose mica collected by Miss Basnett at Broken Hill; (b) Occurrence of vesuvianite in two ways in the one specimen of banded hornfels, from Hartley, N.S.W. : (i) as interbedded grains, (ii) radiating along joint planes associated with sulphides, indicating pneumatolytic action. The bands of the hornfels are vesuvianite-diopside, and wollastonite-orthoclase-diopside. By Mr. L. L. Waterhouse : (a) Vesuvianite in well-formed crystals in bedding planes replacing a calcareous band, associated with pyrite and brown garnet, from Stony River, West Coast, Tasmania; (b) "Fossil Coconut"—a glassy, vesicular, olivine-basalt bomb, from a stream bed near Rabaul; (c) Fresh olivine beach sands with augite, from Bareke, Solomon Islands. By Dr. G. D. Osborne : (a) Hybrid rocks showing reaction between porphyrite and alkali granite, from Lager's Point, near Trial Bay, N.S.W.; (b) A series of specimens showing the effect of shearing upon quartz-orthoclase porphyry from Gundagai, N.S.W. By Mr. J. A. Dulhunty : Teeth remains of *Macropus titan* from the floor of a mature valley at Rockley, N.S.W. By Dr. C. Anderson : A mandible of *Nototherium watutense*, from fresh water beds in the Watut River district, New Guinea, the first discovery of fossil marsupials in New Guinea. By Miss F. M. Quodling : Tuff from Forster, N.S.W., containing organic blebs and streaks, the remains of annelids, possibly *Nereites*. By Dr. A. B. Walkom : Small specimen of a Henbury siderite. Mention made of the failure of the recently carried out magnetic survey to find any substantial mass of iron below the surface. By Mr. H. O. Fletcher : (a) *Eurydesma cordatum* from Braxton beds, Upper Marine, where it occurs plentifully (an

extension of the range) ; (b) Fossil crab, *Prosopon etheridgei*, in concretion from the Cretaceous of Queensland. By Mr. R. O. Chalmers : (a) Rare titano-silicates, benitoite, neptunite, and joaquinite in association with natrolite, from San Benito County, California, U.S.A. ; (b) Suite of rocks, trachybasalt and its alteration products, from No. 1 of the Five Islands, N.S.W. Similar to types described from the Port Kembla quarry.

July 15 : Address by Miss F. M. Quodling, " Experimental Work in X-Ray Crystallography ".

August 12 : Address by Mr. S. W. Carey, " The Geological Background of Wallace's Line ".

September 16 : Address by Mr. C. A. Sussmilch, " The North American Cordillera ".

October 21 : Address by Professor L. C. Graton, Professor of Mining Geology, University of Harvard, U.S.A., " The Use of Hypogene Ores ".

November 18 : Address by Mr. A. H. Voisey, " Structural Problems in the Northern Territory ".

ABSTRACT OF PROCEEDINGS
OF THE SECTION OF
INDUSTRY

Chairman : A. D. Ollé, F.C.S., A.A.C.I.

Visits were made by members of the Section of Industry to the following firms, factories and works during the year ended on December 31st, 1938 :

1938.

May : Messrs. Anderson and Co. Pty., Seed and Plant Merchants, Summer Hill.

June : Ever Ready Company Pty. Ltd., Rosebery.

August : Austral Bronze Co. Pty. Ltd., Alexandria.

September : Australian Paper Manufacturers Ltd., Botany.

October : The N.S. Wales Fresh Food and Ice Company Ltd., Harbour Street, Sydney.

ABSTRACT OF PROCEEDINGS
OF THE SECTION OF
PHYSICAL SCIENCE

Honorary Secretary : C. S. Davis.

1938.

May 4 : Election of Officers.

Mr. D. N. Myers, "The Mechanical Solution of Equations".

June 15 : Mr. R. H. Healy, "The Motion of Electrons in Iodine".

July 6 : Mr. N. F. Roberts, "The Determination of the Energy Levels in Naturally Radioactive Nuclei".

July 27 : Mr. W. McNeil, "Road Traction and the Accident Problem".

August 10 : Professor V. A. Bailey and Mr. J. M. Somerville, "The Study of Electric Wave Propagation by means of Mechanical and Graphical Devices".

September 21 : Dr. Ilse Rosenthal-Schneider, "The Principle of Causality in Physics and Philosophy".

October 12 : Professor V. A. Bailey, "A Brief Method for the Determination of Wave Propagation in the Ionosphere".

October 26 : Dr. D. F. Martyn, "An Experimental Test of the Lorentz Dispersion Theory in the Ionosphere".

November 9 : Professor V. A. Bailey, "On the Possibility of Generating Artificial Auroras".

The average attendance at the meetings was about thirty members and friends.

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OF
NEW SOUTH WALES
FOR
1939
(INCORPORATED 1881)

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Parts I-IV

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† Published April 12, 1940.

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.

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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 $3\frac{1}{2}$ 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 $4 \times 6\frac{1}{4}$ 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.

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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.]

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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	„	„	1878, pp. 324, price 10s. 6d.
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„	LX	„	„	„	1927, „ 492, „
„	LXI	„	„	„	1928, „ 458, „
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„	LXVI	„	„	„	1933, „ 511, „
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- 1937 Baldick, Kenric James, Research Scholar, 19 Beaconsfield-parade, Lindfield.
- 1919 Bardsley, John Ralph, 76 Wright's-road, Drummoyne.
- 1939 P 1 Basnett, Elizabeth Marie, B.Sc., 36 Cambridge-street, Epping.
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- 1926 Bentivoglio, Sydney Ernest, B.Sc.Agr., c/o Tooth & Co. Limited, Sydney; p.r. 52 Crows Nest-road, Wollstonecraft.
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- 1923 Birks, George Frederick, Wholesale Druggist, c/o Potter & Birks Ltd., 15 Grosvenor-street, Sydney; p.r. 42 Powell-street, Killara.
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- 1933 Boan, Robert Farquharson, A.A.C.I., Analyst and Consulting Chemist, 185 Elizabeth-street, Sydney.
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- 1934 Carruthers, H. L., M.B., B.S., 4 Elcho-street, Hamilton, N.S.W.
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- 1919 Cotton, Frank Stanley, D.Sc., Chief Lecturer and Demonstrator in Physiology in the University of Sydney.
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- 1890 Dare, Henry Harvey, M.E., M.Inst.C.E., M.I.E.Aust., 14 Victoria-street, Roseville.
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- 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.
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- 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. Taren Point-road, Taren Point.
- 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., Chief Geologist, North Broken Hill Ltd., Broken Hill, N.S.W.
- 1939 Gascoigne, Robert Mortimer, 30 Charlotte-street, Ashfield.
- 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 W. J., 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.

Elected.

- 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.
- 1933 | Hancock, Francis Charles, B.Sc. (Hons.), Dip.Ed. (*University of Bristol*), c/o Dept. Education, Sydney.
- 1905 | P 6 | Harker, George, D.Sc., F.A.C.I.; p.r. 75 Prospect-road, Summer Hill.
- 1936 | Harper, Arthur Frederick Alan, M.Sc., A.Inst.P., c/o High Commissioner, Australia House, The Strand, London, England.
- 1937 | P 6 | Harradence, Rita Harriet, M.Sc., Research Scholar, c/o Dyson Perrins Laboratory, Oxford University, Oxford, England.
- 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 Castle-reagh-street, Sydney; p.r. 12 King's-road, Vacluse.
- 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. 1 Castlereagh-street, 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, Hurlstone Agricultural High School, Glenfield.
- 1936 | Hirst, Edward Eugene, General Manager, British General Electric Co. Ltd.; p.r. "Springmead," Ingleburn.
- 1928 | Hirst, George Walter Cansdell, B.Sc., A.M.I.E. (*Aust.*), A.M.Inst.T., c/o Chief Mechanical Engineers' 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, "Lindcluden," 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.

Elected.

- 1936 Howie, Sir Archibald, K.B., M.L.C., 7 Wynyard-street, Sydney.
- 1938 P 4 Hughes, Gordon Kingsley, University Lecturer, University of Sydney.
- 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., Box 3010 N.N., G.P.O., Sydney.
- 1929 Jeffrey, Robert Ewen, A.A.C.I., Managing Director, Bardsley's Ltd.; p.r. 9 Greycliffe-avenue, Vacluse.
- 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 5 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.
- 1935 Kelly, Caroline Tennant (Mrs.), 5 Ithaca-road, Elizabeth Bay.
- 1935 Kelly, Francis Angelo Timothy, 5 Ithaca-road, Elizabeth Bay.
- 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. 12 Mackenzie-street, Concord.
- 1939 Lambeth, Arthur James, 49 Church-street, Wollongong.
- 1935 Lawrence, Elizabeth Frances, B.A.
- 1936 Leach, Stephen Laurence, B.A., B.Sc., A.A.C.I., P.O. Box No. 21, Concord.
- 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.

Elected.

- 1934 Leech, William Dale, Director of Research, Australasian Food Research Laboratories, Cooranbong, N.S.W.
- 1936 P 3 Lemberg, Max Rudolf, D.Phil., Biochemist, Royal North Shore Hospital; p.r. 36 Goodchap-road, Chatswood
- 1920 Le Souef, Albert Sherbourne, Curator, Taronga Park, Mosman; p.r. 3 Silex-road, Mosman.
- 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 48 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.
- 1939 Maccoll, Allan, M.Sc., Wesley College, Newtown, N.S.W.
- 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.*, St. Columba's Manse, Guyra.
- 1927 McMaster, Sir Frederick Duncan, kt., "Dalkeith," Cassilis, N.S.W.
- 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., Box 2968 NN, G.P.O., 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, Navy Office, London, England.
- 1912 Meldrum, Henry John, B.A., B.Sc., Lecturer, The Teachers' College, University Grounds, Newtown; p.r. 98 Sydney-road, Manly.
- 1929 P 11 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.
- 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 6 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.
- 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.
- 1938 P 1 Noble, Norman Scott, D.Sc. Agr., M.Sc., D.I.C., Assistant Entomologist, Department of Agriculture, Sydney.
- 1920 P 4 † Noble, Robert Jackson, M.Sc., B.Sc. Agr., Ph.D., Biologist, Department of Agriculture, Box 36A, G.P.O., Sydney; p.r. 32A Middle Harbour-road, Lindfield. (Vice-President.) (President, 1934.)
- 1935 O'Connell, Rev. Daniel J. K., S.J., M.Sc., F.R.A.S., River-view College Observatory, Sydney.
- 1903 † Old, Richard, "Waverton," Bay-road, North 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 5 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. (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, Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern; p.r. "Elgarth," Ranger's-road, Cremorne.
- 1938 Powell, John Wallis, A.S.T.C., A.A.C.I., Managing Director, Foster Clark (Aust.) Ltd., 17 Thurlow-street, Redfern.
- 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 9 Raggatt, Harold George, D.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, 15 Newton-road, Strathfield.
- 1937 P 3 Reuter, Fritz, D.Phil., A.A.I.C., Research Chemist, No. 5, "Wingham," Brighton-boulevard, North Bondi.

Elected.		
1932		Richardson, Henry Elmar, Chemist, Chase-road, Turramurra.
1939	P 2	Ritchie, Ernest, B.Sc., 120 Hastings-parade, North Bondi.
1933		Roberts, Richard George Crafter, Electrical Engineer, 71 Redmyre-road, Strathfield.
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. (<i>Aust.</i>), Chartered Accountant (<i>Aust.</i>), 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.
1935		Savage, Clarence Golding, Director of Fruit Culture, Department of Agriculture, Sydney.
1920		Scammell, Rupert Boswood, B.Sc. (<i>Syd.</i>), 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. (<i>Melb.</i>), 43 Robertson-road, Centennial Park.
1917		Sibley, Samuel Edward, Mount-street, Coogee.
1938		Sheahan, Thomas Henry Kennedy, B.Sc., Chemist, Shell Co. of Australia, Shell House, William-street, Melbourne, C.I, Victoria.
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.
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.
- 1939 Thomas, Mrs. A. V. M., 12 Clifton-avenue, Burwood.
- 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.
- 1932 P 7 Trikojus, Victor Martin, B.Sc., D.Phil., New Medical School, University of Sydney; p.r. 97 Beresford-road, Bellevue Hill.
- 1921 Vicars, Robert, Marrickville Woollen Mills, Marrickville.
- 1935 Vickery, Joyce Winifred, M.Sc., Demonstrator in Botany, University of Sydney; p.r. 6 Coventry-road, Homebush.

Elected.

- 1933 P 4 Voisey, Alan Heywood, M.Sc., Lecturer in Geology and Geography, New England University College, Armidale.
- 1903 P 8 Vonwiller, Oscar U., B.Sc., F.Inst.P., Professor of Physics in the University of Sydney. (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, Killara. (Member from 1910-1913.)
- 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 4 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, Vacluse. (President, 1925.)
- 1936 Wearne, Harold Wallis, 6 Collingwood-street, Drum-moyne.
- 1920 P 39 Welch, Marcus Baldwin, B.Sc., A.I.C., Senior Research Officer, Forestry Commission of N.S.W., 96 Harrington-street, Sydney. (Hon. Treasurer.)
- 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 Wenzholz, Harold, B.Sc.Agr., Director of Plant Breeding, Department of Agriculture, Sydney.
- 1935 Wentworth, William Charles, 17 Wentworth-street, Point Piper.
- 1881 †Wesley, W. H., London.
- 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.

Elected.

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, M.Sc., A.Inst.P., F.R.A.S., Assistant Astronomer, Sydney Observatory; p.r. 4 Ormond-street, Ashfield.
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.

1939		Chapman, Frederick, A.L.S., F.R.S.N.Z., F.G.S., "Crohamhurst," 17 Threadneedle-street, Balwyn, Victoria.
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.
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. <i>Edin.</i> , F.R.S., Professor of Anatomy in the University of Cambridge; p.r. 31 Grange-road, Cambridge, England.

OBITUARY 1939-1940.

Elected.

- 1878 Alfred Paxton Backhouse.
1888 Walter Blaxland.
1923 Lindsay Duncan Cameron.
1882 Samuel Cornwell.
1912 Louis Albert Curtis.
1916 Walter William L'Estrange.
1879 John Lane Mullins.
1935 John Hubert Plunkett Murray.
1924 Harvey Nickoll.
1930 William J. O'Leary.
1917 William Joseph Spruson.
1891 Percy Moore Wood.
-

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.)
1939. "Pioneers of British Geology." By Sir John S. Flett, K.B.E., D.Sc., LL.D., F.R.S.

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.R.S.N.Z., 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.
- 1939 C. A. Sussmilch, F.G.S., F.S.T.C., 11 Appian Way, Burwood, N.S.W.

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."

Awarded.

- 1894 R. H. Mathews, L.S., Parramatta, for paper entitled "The Aboriginal Rock Carvings and Paintings in New South Wales."
- 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.
- 1938 Frank Macfarlane Burnet, M.D. (*Melb.*), Ph.D. (*Lond.*), The Walter and Eliza Hall Institute of Research in Pathology and Medicine, Melbourne.

 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 JULY 3, 1939

VOL. LXXIII

PART I

JOURNAL
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OF THE
ROYAL SOCIETY
OF
NEW SOUTH WALES

FOR
1938
(INCORPORATED 1881)

PART I (pp. 1 to 40)

OF
VOL. LXXIII

Containing Presidential Address and Papers read
from March to May, with Plate I.

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



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1939



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PRESIDENTIAL ADDRESS

By PROFESSOR J. C. EARL, D.Sc., Ph.D.

(Delivered to the Royal Society of New South Wales, April 5, 1939.)

PART I. GENERAL.

As has been the custom for a number of years, a brief summary will first be given of the main events concerning the Royal Society of New South Wales during the past year.

The number of papers read during the year was twenty-nine, a considerable falling off in numbers from the record established in the previous year. There has, in consequence, been less demand on the funds of the Society for printing and publishing the Journal.

It was decided on the recommendation of a sub-committee appointed to enquire into the matter of publication, that in future the Journal and Proceedings should be issued in unbound quarterly parts, on March 1st June 1st, September 1st and December 1st, the decision to take effect from the beginning of the 1939 volume.

The Clarke Memorial Medal for 1939 has been awarded to Mr. C. A. Sussmilch for his contributions to geological science over many years.

The Annual Dinner for 1939 was held at the Restaurant Annexe of Messrs. Farmer and Company. The Society was honoured by the presence of the State Governor, His Excellency the Lord Wakehurst. Sir Henry Manning was also a guest, having taken the place at short notice of the Honourable B. S. B. Stevens, Premier of New South Wales, who was indisposed. Eighty-seven members and their guests were present at the dinner.

The Balance Sheet shows that the financial position of the Society has improved during the year. This is due in part to the continuance of the Government grant of £400 for the year, and in part to the decrease in the amount of

arrears of subscriptions which resulted from the efforts of the honorary treasurer.

The Walter Burfitt Prize and Medal were awarded in December, 1938, to Dr. F. M. Burnet, of the Walter and Eliza Hall Institute of Research, Melbourne. The presentation of the medal was made at an appropriate sectional meeting of the Australian and New Zealand Association for the Advancement of Science at Canberra.

The Popular Lectures delivered during the winter season of 1938 were well attended both by members and their friends, as well as by the general public.

The Library has been made use of by a number of members and accredited readers, while books have been lent on request to the universities and scientific institutions both within and beyond the State borders. Additions have been made to the shelving, for greater convenience in the arrangement of current periodicals.

In accordance with a previous resolution, the annual general meeting of the Society will now take place in April, concurrently with the first general monthly meeting of the year. The necessary alterations have been made in the wording of the rules.

The membership of the Society stands at the present time at 266 ordinary members and seven honorary members. This is rather a considerable decrease in membership since 1937, when the report showed a membership of 300. Twelve members were elected during the year, and we lost seven members by resignation and ten by death, including four who had belonged to the Society for periods of 51, 52, 60 and 60 years respectively. The members whose deaths we regretfully record are :

ARTHUR BAYLEY, who died on July 11, 1938, had been a member since 1935. He was head of the tanning business of J. Bayley and Sons; shortly after the Federation of the Commonwealth Mr. Bayley started a branch in Australia of his New Zealand leather business, and at the time of his death the business had grown until it employed 400 men. Mr. Bayley belonged to the Rotary Club.

WALTER BLAXLAND, who died on February 27, 1939, had been a member of this Society for fifty-one years. Dr. Blaxland was a member of one of Australia's pioneering families, being a grandson of Gregory Blaxland, who with Wentworth and Lawson was the first to succeed in the difficult crossing of the Blue Mountains. In 1916 Dr.

Blaxland volunteered as an honorary medical officer at Randwick Military Hospital, where he remained until 1920.

JAMES B. BROWN, who died on July 9, 1937, was elected a member of the Society in 1906. He was born in Berwick-on-Tweed in 1855, educated at Clergy Jubilee School, Newcastle-on-Tyne, and at Rutherford College, and later attended Professor Goodeve's lectures in applied mechanics. In 1874 he won the Queen's Prize in the examination held by the Science and Art department of the Committee of Council on Education. Until leaving England in 1884, he was assistant to Dr. Evers at the Elswick Institute attached to Sir William Armstrong's works. In 1885 the Board of Technical Education appointed him teacher of mechanical and geometrical drawing at Granville, and, as the work grew, he was appointed Resident Master of Granville Technical School, later College; when he retired from that position in 1921, he left a staff of eighteen teachers. In 1928 he settled in Melbourne, where he remained until his death.

LINDSAY DUNCAN CAMERON died in March, 1939; he had been a member of the Society since 1923.

HARRY CHAMBERS KENT, who died on August 9, 1938, had been a member of the Society for fifty-one years. Mr. Kent was born in Devonshire in 1852, and was brought to Sydney in the following year. He was educated at Camden College, of which his father, the Rev. S. C. Kent, was headmaster. Later he gained the M.A. degree at the University of Sydney. After serving his articles, Mr. Kent in 1882 started practice as an architect, and some years later took Mr. H. E. Budden into partnership. The partnership continued until 1919, and at that date Mr. Kent was associated with Mr. Hugh H. S. Massie. For many years Mr. Kent held the position of honorary secretary of the Children's Hospital, and was also connected with other charitable and religious organizations.

JOHN LANE MULLINS died on February 24, 1939, after having been a member of the Royal Society for sixty-one years. Mr. Mullins was born in Sydney eighty-one years ago, and had a brilliant scholastic career at the University, graduating M.A. when only twenty-one years of age, after being educated at St. Mary's College, Lyndhurst, and St. John's College. He was admitted as a solicitor of the Supreme Court in 1885, and was called to the Bar in 1930. Mr. Mullins was associated with some of the largest

commercial institutions in New South Wales. He held a number of honorary offices, namely treasurer of St. Mary's Cathedral, honorary secretary for twenty-five years of St. Vincent's Hospital, and later its honorary treasurer. He was secretary of the Society of Artists, a trustee of the National Art Gallery, and later its President, President of the Australian Ex-Libris Society, and of the Society of Australian Limited Editions. He himself possessed one of the largest and most valuable collections of bookplates in the Commonwealth. Mr. Mullins also played his part in civic life, for from 1900 to 1912 he was an alderman of the City Council, chairman of the Finance Committee from 1902 to 1904, and again in 1910. In 1917 he was appointed to the Legislative Council, and remained a member of the Chamber for seventeen years.

PROSPER CHARLES TREBECK died on August 19, 1938 ; he had been a member of the Society since 1879. He was connected with the pastoral industry all his life, and when he retired was principal of the firm of Trebeck, Son and Co., stock and station agents. He took an interest in many organisations, including the Royal Society for the Prevention of Cruelty to Animals, the Hospital Saturday Fund, and was formerly one of the treasurers and a vice-president of the Royal North Shore Hospital.

GEORGE BEGG VICKERY, who died on June 18, 1938, had been a member of the Society since 1882. Mr. Vickery was 72 years of age. He was prominently associated with the coal mining industry, and was Chairman of Directors of Coal Cliff Collieries from its formation in 1909, and for many years was a member of the board of management of the Southern Coal Owners' Agency, and a director of B. Byrnes Limited. He was a member of the Southern Colliery Proprietors' Association and chairman for several years, until 1927. For more than thirty years he was managing director of E. Vickery and Sons Limited.

FRED WALSH died on November 12, 1938 ; he had been a member of the Society since 1903. Mr. Walsh was formerly Consul-General for Honduras in Australia and New Zealand.

PERCY MOORE WOOD died on February 27, 1939. Dr. Wood had been a member of the Society since 1891. He was in practice for many years at Ashfield, and had gained the qualifications of M.R.C.S. and L.R.C.P. in London, where he was for some time attached to Guy's Hospital.

PART II.

THE USE AND MISUSE OF SCIENCE.

In these days of specialisation we are always in danger of losing sight of some of the general attributes of science as a whole. In fact one might say that it goes beyond being a danger ; we have to a large extent suffered the loss. Some three centuries ago Francis Bacon gave the warning, "Another error . . . is that after the distribution of particular arts and sciences, men have abandoned universality or *philosophia prima* ; which cannot but cease and stop all progression ".⁽¹⁾ In more modern terms, what Bacon would say is that it is a mistake for scientific specialists to ignore the general foundations of science, a mistake which will lead to stagnation. Whether we agree entirely with this statement or not, probably most of us would acknowledge that there is some truth in it.

For this reason I wish to use this opportunity, not for giving you a technical discourse on the branch of science in which I work but for directing your attention to some more general matters which I consider to be important.

The present period in the world's history is often called "the scientific age". The reason for this is quite apparent because never before, so far as we have any record, has so much practical use been made of knowledge. Our forefathers discovered many things about the earth and its contents and about the universe of which it forms a part. Many of their discoveries had no obvious use apart from the fact that they extended the bounds of knowledge. They were of interest only to the few who concerned themselves with intellectual matters. Many a discovery has in the past lain unused and almost unknown for years. Coal gas furnishes an example. It is recorded that in 1690 a Yorkshire clergyman, Dr. Clayton, collected coal gas in bladders and entertained his friends by puncturing the bladders and lighting the issuing gas. It was not until 1792 that the first practical use was made of gas for lighting purposes by William Murdoch. In 1807 it was seriously applied for street lighting purposes in London. A more recent example is that of the bakelite resins. The resinous products formed from formaldehyde and phenol were known to chemists in 1891 but it was not until 1908 that Baekeland used the observation to found the now extensive plastics industry.

Discovery is still proceeding. Scientific men are still at work extending our knowledge of our environment. Every human being is something of a scientist because he learns by experience what he can do and what he cannot do. But always throughout the ages there have been men who have wanted to go beyond simple everyday experiences. They have questioned the truth of accepted tradition and subjected it to the test of deliberate experiment. They have wondered about the causes behind well known natural phenomena. They have sought to understand the mechanism of the universe. The earlier natural philosophers relied more on speculative thought than on observation and experiment. Progress at that stage was slow. Some three hundred years ago saw the dawn of the era of experimental science and the boundaries of knowledge commenced to widen rapidly. Accurate observation took the place of interminable discussions of which the basis was no more than a clash of opinions. The value of systematic and accurate recording of results of observations came to be recognised and each generation was able to build on the structure left by the preceding one. Instruments were devised to assist men to see in greater detail things of which the outline only had been visible before.

So it came to be that men recognised that there is an essential unity in things, that there is order in nature and that natural phenomena occur in accordance with certain natural laws. The aim of scientific study is to find out all about this order in nature. Once it is known what general principles or laws are behind the working of nature, immense power is placed at the disposal of humanity. Although extensive, this power is nevertheless limited, because men cannot change these natural laws or indeed prevent their operation in any great degree.

The use of our increased knowledge has led to great changes in the way of living for the whole human race. So great are the changes that a vague impression seems to be abroad that science has put into the hands of men a controlling weapon, a big stick with which nature may be beaten into obedience to men's wishes. In many writings which purport to survey the political and social condition of the world today references are made to man's "control of nature" and the uses and misuses he makes of his power. One such recent example may be quoted, but it is only typical of many. W. Macneile Dixon in his extraordinarily interesting book "The Human Situation" appears to

accept for granted this attitude of control.⁽²⁾ He says, "While our control over nature's energies approaches the miraculous, anarchy reigns in the moral and æsthetic, as well as in the intellectual sphere". It is obvious from the rest of the book that the phrase "control over nature's energies" is not intended to mean what it says. In a non-scientist perhaps some looseness of expression on such matters may be overlooked. But one is astonished to find similar phraseology in scientific discussions. At the recent Canberra meeting of the Australian and New Zealand Association, one prominent scientist is reported to have referred to "man's increasing power over the forces of nature" and another to "the vile misuse men were willing to make of the control over nature which had been put into their hands by the labours of hosts of scientific workers".⁽³⁾ Language of that kind is likely to imply to the casual reader or hearer that scientific men can have a sort of dictatorial influence over natural occurrences. Actually the position is very different. Analysis of even the greatest achievement that can be regarded as resulting from the application of scientific knowledge, shows only that it is nature and not man who is the dictator. The achievement involves two factors. The first is the knowledge that under certain circumstances a known natural phenomenon will occur. The second is the ability of man to arrange the stage so that the occurrence takes place when and where he wishes. Knowledge alone will accomplish nothing; action must be added to it. On the other hand, action not guided by knowledge is as likely to lead to disaster as to benefit.

A simple example may illustrate the point. It is known that an electric current can be used to produce certain effects. It is known that some materials are conductors of electricity and some are not. If we desire to have the benefit of the effect of the current of electricity flowing from one point to another we have to use a conductor to make the connection. Our knowledge of how nature works guides our action. If we refuse the guidance and use a non-conductor, we do not achieve the desired result.

It has been said that knowledge is power. Knowledge may be power but it remains inactive until a conscious effort is made to use it. Then what is actually done is to arrange the stage for nature to perform. The result of nature's performance depends to some extent on how the stage is arranged. A charge of gunpowder of suitable

size in a cardboard casing and fitted with a fuse makes a harmless cracker; a larger charge packed into a more resistant container and similarly fitted with a fuse may be used to make havoc in its immediate neighbourhood. The same natural phenomenon occurs in each case but the setting of the stage has been different.

This capacity to use nature's performances intelligently places tremendous power in the hands of men. By it men become active agents in the process of evolution. We can use the power we have destructively or constructively. It is a great responsibility and cannot be regarded lightly. We cannot evade it without discarding knowledge. People have sometimes been appalled at the prospect and have suggested suspension of scientific work for fear that the burden of responsibility shall become too great to be borne. "He that increaseth knowledge increaseth sorrow", said a writer of old,⁽⁴⁾ and there are those today who hold a similar view. This attitude of pessimism is hardly justified. Increasing knowledge has brought in its train countless benefits as well as the potentialities of evil. It is a question whether we can have the one without the other. We may be in the position of the would-be purchaser referred to by Sir William Bragg.⁽⁵⁾ The auctioneer said to the purchaser, "Sorry, sir, but if you want the parlour lamp you've got to take the garden roller. They're in the same lot".

After all, we can use or misuse most of the things we have. Our conduct must be determined by some kind of motive. Some would have us believe that it is all a matter of natural instincts, heredity or influence of environment—in other words that we have no real power of choice. Others, and I am on their side, while not being able to explain why we have the power to choose, believe that we have it and should use it. There is no reason why scientific men should not join with the rest of humanity in attempting to control the use of knowledge. They are possibly more fitted by training and temperament to disentangle their motives from their interests than people engaged in commerce, industry or politics. But they cannot assume the responsibility of concealing discoveries they have made because they are capable of being wrongly used. Moral issues arise in the use of everything, and indeed in every human action. A discussion of the basis of such issues, although interesting, is outside the scope of an address of this kind.

To return to the more tangible side of our discussion : whether for constructive or destructive purposes we can and do use science. There are, in research organisations throughout the world, men well versed in scientific knowledge engaged in turning that knowledge to account, either in producing some new thing to make the lives of their fellow men easier or more enjoyable, or in improving the production of some widely used article to make it cheaper or better. Sometimes such work is carried out directly in connection with industry, sometimes in research institutions especially established for fostering the use of science in medicine, agriculture, and so on. This effort, widely spread and justified overwhelmingly by the results it has given, is usually referred to as scientific research, although it has not as its direct aim the extension of fundamental knowledge. It is valuable and necessary work, but it does seem desirable to distinguish it in some way from another kind of scientific research work, concerned with what is often referred to as " pure " science. For the purposes of the following discussion I will call the kind of research associated with the use rather than the extension of knowledge, secondary scientific research. That kind of work directed towards the extension of knowledge as such, I will call primary scientific research.

We are set in the midst of a vast and complex organism—in fact we form part of it—which we by no means completely understand. What we have been able to find out leads us to the conclusion that it has an essential unity and that each working part is linked with countless others. There are still many obscure corners into which we have not been able to penetrate. No doubt, too, there are things directly under our eyes which are nevertheless beyond our powers of observation. Many familiar things on closer examination reveal interesting features which we did not dream they possessed. We have passed in the course of generations from the macroscopic to the microscopic, to the ultramicroscopic examination of things, from the bulk to the molecule, to the atom, to the electron, proton, and neutron. A great deal of scientific enquiry consists of looking at things and events more closely.

The primary scientific work of discovery for its own sake has engaged the attention of men in every generation. Nowadays, the increasing complexity of the tasks involved has, to a large extent, eliminated the entirely independent worker. The universities and other academic institutions

have resources and man-power at their disposal which very few independent investigators can have. If primary scientific research is to continue we have to trust the managements of such institutions to foster it. Before making any criticism as to the way in which the responsibility is being undertaken, it is as well to recognise the difficulties. A modern university is expected to perform many duties. The training of recruits for the learned professions is one expensive and laborious task. The maintenance of the cultural traditions of the older universities by providing for the study of philosophy, philology and literature is assumed to be a primary necessity. The desire for an understanding of the basis of the modern social order calls for departments of economics, history, and the like. Added to all these demands comes that for the support and encouragement of primary scientific research. It is perhaps not surprising that a demand which has not the weight of a strong outside influence is sometimes put on one side.

When the Royal Society of London was founded in the middle of the seventeenth century, universities did not consider that the encouragement of scientific research was part of their task. It was the active ferment of science in the outside world that stimulated the universities in later years to establish chairs of science. There are few of those concerned in primary scientific research in the universities of Australia who would not agree that some outside stimulation would be helpful here.

There are numerous and weighty reasons why people in general should be interested in maintaining active schools of primary scientific research. In the first place, there are some ways in which the basic knowledge resulting from primary scientific research may be compared to the raw materials available from natural sources. As everyone knows, there are directions in which the resources of the earth seem to be approaching exhaustion. It is recognised that foresight is necessary to avoid dislocation of our civilisation. We have to seek substitutes for petroleum or abandon internal combustion engines. We have to embark on schemes of reafforestation to counter the destruction of our natural forests, and so on. If we wish to continue to benefit from the application of knowledge to meet human needs, it seems obvious that we should be constantly adding to our store.

Much is said about "culture", a rather mysterious thing the absence of which causes grief to some worthy people. Some such feel that it is associated exclusively with a knowledge of ancient or modern literature, or with philology, or with philosophy, or some other really respectable branch of study. Science, on the other hand, is looked on as rather deficient in cultural value. Yet the languages of men and the thoughts of men as subjects of study have no special superiority; on the contrary they are rather narrow in their scope. The environment in which men live and the evolutionary processes by which men have come to their present state are surely just as worthy and just as elevating matters on which to exercise our wits. Culture in the universities is more likely to be fostered than to be extinguished as a result of an increase in primary scientific research.

The results of this kind of work seldom furnish good talking points. The ultimate applications of any particular fundamental discovery can seldom be foreseen. All that can be said usually is that it adds to knowledge. Faraday could hardly have imagined that his electrical discoveries were going to be the basis of the modern power station. Dalton did not realise that he was laying the foundation for an extraordinary development in the use of the earth's resources. These pioneers and many others were aiming at the extension of knowledge and the primary scientific workers of today are doing exactly the same.

We must ask ourselves seriously whether our present system of fostering primary scientific research is adequate. Are the fires burning brightly enough, or are we putting so many secondary scientific pots on to boil that some of them must necessarily remain cold? In a long range policy of national development we must ensure that we are not entirely dependent on other countries for our primary knowledge. We have seen the wonderful success achieved here in Australia by government encouragement of secondary scientific research. The Council for Scientific and Industrial Research is a national institution of which all Australians should be proud. The more fundamental work in science is neither organised nor financially supported on anything like the same scale. Yet it is generally recognised that those who are to work in the secondary research field are better equipped for their task if they have had some actual contact with primary scientific research. Later they are to use fundamental knowledge as one of

the principal instruments in their own work, and some knowledge of the inner construction of the instrument helps towards its intelligent use. It is true that recently financial assistance for research in the universities of Australia has been provided by the Commonwealth Government through the Council for Scientific and Industrial Research. That assistance has been timely and valuable. But there needs to be added to it a more general recognition that the advance of knowledge by research is a primary duty of the universities. It is not to be regarded as a pleasant way the teaching staff has of spending its spare time, if any; it is one of the primary objectives for which the universities exist. Positive organisation for the effective carrying out of this objective is almost entirely absent. The tendency to foster secondary rather than primary research in the universities with the resources now available is dangerous; the claims of the latter require more energetic support from within and without.

In urging that a larger and keener interest should be taken in fundamental work, I do not wish to give the impression that secondary scientific work is to be regarded as less important. The fact is that this age in which we live does not need to be urged to use either knowledge or material things. It is an age of using rather than one of discovery. The two spheres of activity, discovery and the use of it, are closely inter-linked. Knowledge has to be acquired to be used, but in being used it becomes better understood, and new directions for the pursuit of knowledge are indicated.

The present disturbed state of international affairs has for us in Australia a profound significance. We wish to retain for our own use and under our own system of government a very large territory. Up to the present we have been slowly finding out what its potentialities are. The urge of economic necessity has not forced us to an intensive study of our natural resources. Yet the work that has been done has shown us that in many ways Australia is unique, especially in the matter of its fauna and flora. Over and over again, in the particular field of work in which I am engaged, it has been found that Australian natural products have a quite exceptional interest. It is hardly a matter for pride that much of the more fundamental work underlying the chemistry of Australian plant products is being done overseas and much

more is remaining untouched. The reason is the simple one that the trained man-power and the necessary facilities are not available. One of the biggest scientific problems in the world is calling for our attention—Australia and its contents. It is our duty to treat this problem seriously.

A systematic and sustained attack on the problem involves the recognition of both primary and secondary scientific research as national activities. All the accurate knowledge acquired would not be immediately useful, but, as I have been trying to emphasise, discovery must precede the use of discovery.

This Society may take its part in the matters I have mentioned. It already provides a very valuable means of publishing results but it could go further. The interpretation of scientific achievement in other terms than its commercial usefulness is necessary. The encouragement of mutual understanding between specialised workers from all branches of science is another urgent requirement. Above all, to produce an active intellectual ferment in the community would be of incalculable benefit.

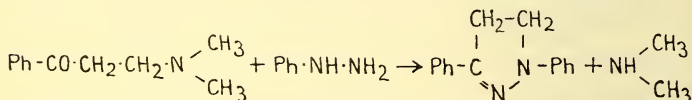
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- (1) *The Advancement of Learning*, Book I.
 - (2) *The Human Situation*. W. Macneile Dixon. Australian Edition, 1938, p. 34.
 - (3) *Australian Journal of Science*, 1939, 1, 116, 118.
 - (4) *Ecclesiastes*, I, 18.
 - (5) *Science, Friend or Enemy?* Introductory chapter to Julian Huxley's "Scientific Research and Social Needs".
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RESEARCHES ON INDOLES.*

PART IX. THE REACTION OF PHENYLHYDRAZINE WITH
"MANNICH" BASES.By RITA H. HARRADENCE, M.Sc.,
and FRANCIS LIONS, B.Sc., Ph.D.*(Manuscript received, March 22, 1939. Read, April 5, 1939.)*

The formation of derivatives of pyrazoline by interaction of phenylhydrazine and "Mannich" ketonic tertiary bases has been frequently observed. Thus, Jacob and Madinaveitia (*J.C.S.*, 1937, 1929) noted the formation of 1:3-diphenylpyrazoline (I) when phenylhydrazine reacted with phenyl β -dimethylamino ethyl ketone, dimethylamine being extruded; and that phenylhydrazine and 1-dimethylaminobutan-3-one in acetic acid solution formed an inter



I

mediate substance, which gave 1-phenyl-3-methyl pyrazoline when treated with alcoholic hydrogen chloride. Levy and Nisbet (*J.C.S.*, 1938, 1053) also have recorded the formation of a pyrazoline when phenyl hydrazine was reacted with any of the Mannich bases derived with dimethylamine, diethylamine, di-*n*-propylamine or piperidine from 2-acetyl-4-phenyl thiazole; whilst the present authors observed (*THIS JOURNAL*, 1939, 72, 233-248) the formation of pyrazolines from phenylhydrazine and several aryl β -morpholino ethyl ketones. It should also be mentioned that Mannich and Bauroth (*Berichte*, 1924, 57, 1108) prepared 1-phenyl pyrazoline-3-propionic acid phenyl hydrazide by interaction of phenylhydrazine and 4-keto-6-dimethylamino hexoic acid hydrochloride at 100°.

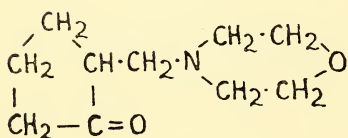
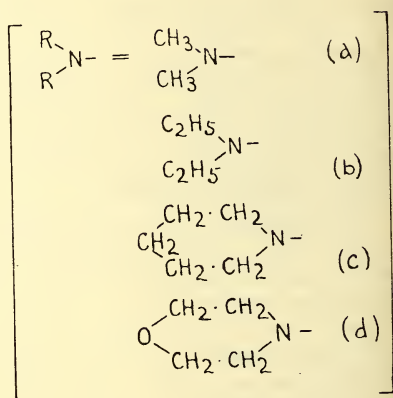
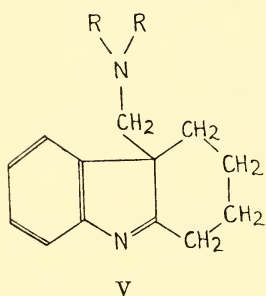
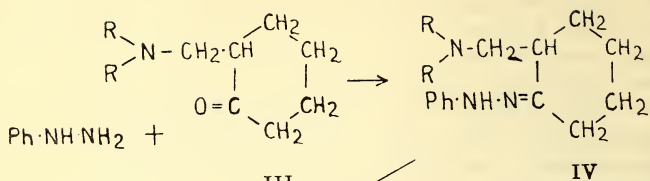
* For Part VIII of this series, see *THIS JOURNAL*, 1939, 72, 221-227.

On the other hand, apparently the only recorded reference to the action of phenyl hydrazine on Mannich bases derived from cyclic ketones is that to the work of Mannich and Hönig (*Arch. Pharm.*, 1927, 265, 598), who showed that under somewhat drastic conditions—heating together at 170°—phenylhydrazine and 2-dimethylamino methyl cyclohexanone react with formation of products such as tetrahydrocarbazole, ammonia, aniline, and piperidine. The formation of a phenylhydrazone of the ketonic base was not recorded. Because the phenylhydrazones of ketones of the type $R - CO - CH < \begin{matrix} R^1 \\ R_{11} \end{matrix}$ are well known to cyclise with great ease to indolenines (cf. e.g. Plancher, *Berichte*, 1898, 31, 1496; Gogin, *Monatsh.*, 1906, 27, 731; Jennisch, *Monatsh.*, 1906, 27, 1223; Hughes and Lions, *THIS JOURNAL*, 1937-8, 71, 494-502), it appeared to the authors that a Mannich base of the type of (III) should react with phenylhydrazine to give first a phenylhydrazone, which ought then to be capable of cyclisation with acid to a substituted tetrahydrocarbazolenine.

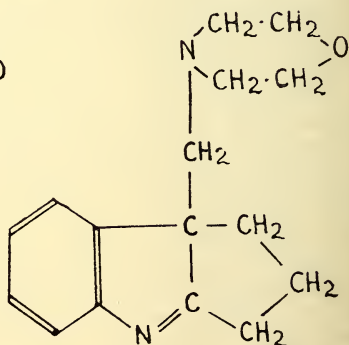
Experiments have now confirmed the accuracy of this contention. When phenylhydrazine reacts in the cold with various Mannich bases (III) derived from cyclohexanone, water is split out, with simultaneous evolution of heat and formation of oily phenylhydrazones (IV). Of these, the phenylhydrazone of 2-morpholino methyl cyclohexanone (IV*d*) has been obtained as a yellow crystalline substance melting at 112°.

Rapid passage of dry hydrogen chloride into absolute ethyl alcoholic solutions of the phenylhydrazones (IV) leads to the occurrence of vigorous reactions, separation of crystalline ammonium chloride and simultaneous formation of the corresponding 11-disubstituted aminomethyl-1:2:3:4-tetrahydrocarbazolenines (V), which usually remain in solution as their hydrochlorides. However, the hydrochloride of (V*d*) crystallised out with the ammonium chloride in the crude reaction liquid. The bases corresponding to (V*e*) and (V*d*) were readily obtained crystalline, but (V*a*) and (V*b*) were oils which were characterised by their crystalline picrates.

Further experiments showed that 2-morpholino methyl cyclopentanone (VI) also readily forms a phenylhydrazone which cyclises with alcoholic hydrogen chloride to the crystalline indolenine base (VII)-3-morpholino-methyl-2:3-trimethylene indolenine.

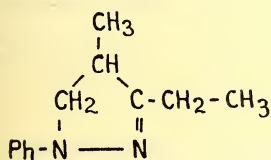


VI

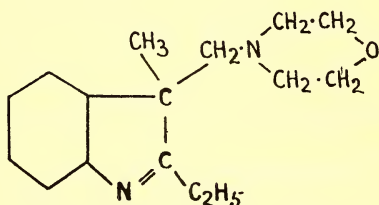


VII

However, when a further investigation was carried out with the Mannich base 2-morpholino methyl-pentan-3-one (VIII), although this reacted readily enough with phenylhydrazine to give an oily phenylhydrazone, it was found that rapid saturation of an alcoholic solution of this substance with dry hydrogen chloride led to deposition of a precipitate containing both ammonium chloride and morpholine hydrochloride, thus indicating the formation of both 1-phenyl-3-ethyl-4-methyl pyrazoline (IX) and 2-ethyl-3-methyl-3-morpholino methyl indolenine (X). The amount of material available did not permit of the isolation of either of these in the pure condition. The presence of (IX) was almost conclusively demonstrated by the strong Knorr pyrazoline reaction of the product.



IX



X

EXPERIMENTAL.

2-Morpholinomethyl cyclohexanone phenylhydrazone.

Equimolecular proportions of 2-morpholinomethyl cyclohexanone and phenylhydrazine were mixed in the cold. Reaction occurred with heat evolution and splitting out of water. The product solidified after addition of water and scratching. Recrystallised from petroleum ether it came out in pale yellow prisms melting at 112°.

Found: N=14.2%; calculated for $C_{17}H_{25}ON_3$, N=14.6%.

11-Morpholinomethyl-1:2:3:4-tetrahydrocarbazolenine.

Morpholinomethyl cyclohexanone phenylhydrazone (20 g.) was dissolved in absolute alcohol (100 c.c.) and a rapid stream of dry hydrogen chloride passed through the solution. After about ten minutes a vigorous reaction occurred with ebullition and precipitation of a white solid. After further brief passage of hydrogen chloride the

mixture was allowed to stand half an hour, then cooled in ice and filtered. The residue consisted of a mixture of ammonium chloride and the hydrochloride of *11-morpholinomethyl-1 : 2 : 3 : 4-tetrahydrocarbazolenine*. The latter (15 g.) was obtained by recrystallisation from alcohol in colourless plates, m.p. 211°.

Found : N=9.2% ; calculated for $C_{17}H_{23}ON_2Cl$, N=9.1%.

The *free base* was recrystallised from petroleum ether and obtained as colourless prisms, m.p. 112°. (Mixed m.p. with 2-morpholinomethyl cyclohexanone phenylhydrazone was 106°.)

Found : N=10.6% ; calculated for $C_{17}H_{22}ON_2$, N=10.4%.

The *picrate*, precipitated from alcohol solution and recrystallised from dioxan, formed shining orange needles, m.p. 193°.

Found : C=54.9, H=5.0, N=13.5% ; calculated for $C_{23}H_{25}O_8N_5$, C=55.3, H=5.0, N=14.0%.

11-Piperidinomethyl-1 : 2 : 3 : 4-tetrahydrocarbazolenine.

2-Piperidinomethyl cyclohexanone (28 g.) and phenylhydrazine (16 g.) were mixed ; evolution of heat occurred and water separated, but crystallisation did not take place on standing overnight, nor could it be induced. The phenylhydrazone was therefore taken up in ether and dried. After removal of the ether it was dissolved in absolute alcohol and cyclised directly with dry hydrogen chloride. A vigorous reaction occurred after about ten minutes, with darkening of the solution and separation of ammonium chloride. The carbazolenine hydrochloride did not separate as in the case of the morpholino compound. The reaction mixture was poured into water, extracted with ether to remove non-basic materials, basified, and the product extracted with ether. After drying and removal of the ether a viscous dark brown oil remained, which crystallised after seeding with the morpholino compound. The gummy material was removed as far as possible on a porous tile and the residue on recrystallisation from methyl alcohol gave colourless prisms, m.p. 95°.

Found : N=10.4% ; calculated for $C_{18}H_{24}N_2$, N=10.4%.

The *picrate* precipitated from alcohol as a gum which soon solidified on scratching. It was purified by recrystal-

lisation from dioxan, and then formed small orange needles m.p. 207°.

Found : N=13.9% ; calculated for $C_{24}H_{27}O_7N_5$, N=14.1%.

11 - Diethylaminomethyl - 1 : 2 : 3 : 4 - tetrahydrocarbazolenine
(V ; R=C₂H₅).

This was prepared by a method similar to that described for the piperidino analogue. The viscous dark brown oil obtained on evaporation of the ethereal solution showed no sign of crystallisation. However, it gave a gummy *picrate*, which crystallised on scratching, and after recrystallisation from alcohol formed dark orange needles, m.p. 158°.

Found : Picric acid=46.8% ; calculated for $C_{23}H_{27}O_7N_5$, picric acid=47.2%.

[Picric acid was estimated by the method of Bolliger, (THIS JOURNAL, 1934, 68, 240).]

11 - Dimethylamino - 1 : 2 : 3 : 4 - tetrahydrocarbazolenine
(V ; R=CH₃).

Prepared by the method described for the piperidino compound, this was obtained as a dark brown oil which partially crystallised after some days' standing in contact with a crystal of morpholino-methyl tetrahydrocarbazolenine. It could not be purified, however, but gave a *picrate*, which on recrystallisation from alcohol formed pale yellow plates, m.p. 175°.

Found : Picric acid=49.8% ; calculated for $C_{21}H_{23}O_7N_5$, picric acid=50.1%.

2-Morpholinomethyl cyclopentanone phenylhydrazone.

2-Morpholinomethyl cyclopentanone (15 g.) and phenylhydrazine (9 g.) were mixed and allowed to stand. They reacted with evolution of heat and separation of water and the phenylhydrazone gradually crystallised out. Recrystallised from petroleum ether it formed colourless prisms which became yellow on exposure to light, m.p. 103°.

Found : N=15.2% ; calculated for $C_{16}H_{23}ON_3$, N=15.4%.

The *picrate* recrystallised from alcohol, formed orange needles m.p. 160°.

Found : Picric acid=45.2% ; calculated for $C_{22}H_{26}O_8N_6$, picric acid=45.6%.

BB—April 5, 1939.

3-Morpholinomethyl-2 : 3-trimethylene indolenine.

2-Morpholinomethyl cyclopentanone phenylhydrazone (10 g.) was dissolved in absolute alcohol (50 c.c.) and the solution saturated with dry hydrogen chloride. The hydrochloride of the phenylhydrazone crystallised out almost immediately, but on further passage of hydrogen chloride the solution darkened and the crystalline form changed, a mixture of ammonium chloride and *3-morpholinomethyl-2 : 3-trimethylene indolenine hydrochloride* being precipitated. The latter on recrystallisation from aqueous alcohol was obtained as colourless needles with a faint violet tint, m.p. 241°.

Found : N=9.6% ; calculated for $C_{16}H_{21}ON_2Cl$, N=9.6%.

The *free base*, recrystallised from aqueous alcohol, formed colourless needles, m.p. 103°. (Mixed m.p. with 2-morpholinomethyl cyclopentanone phenylhydrazone was 95°.)

Found : N=10.7% ; calculated for $C_{16}H_{28}ON_2$, N=10.9%.

The *picrate*, on recrystallisation from alcohol, was obtained as orange red needles, m.p. 194°.

Found : N=14.6% ; calculated for $C_{22}H_{23}O_8N_5$, N=14.4%.

2-Morpholinomethyl pentan-3-one.

Diethyl ketone (22 g.), paraformaldehyde (7.5 g.) and morpholine hydrochloride (31 g.) were refluxed on the water bath for five hours. The hydrochloride was then precipitated with ether and filtered off. Recrystallised from acetone it formed colourless needles, m.p. 131°.

Found : N=6.4% ; calculated for $C_{10}H_{20}O_2NCl$, N=6.3%.

The *picrate*, recrystallised from alcohol, formed beautiful yellow needles, m.p. 132°.

Found : Picric acid=55.5% ; calculated for $C_{16}H_{22}O_9N_4$, picric acid=55.3%.

The *free base* was isolated in the usual manner and distilled in high vacuum. It was thus obtained as a colourless liquid (23 g.), boiling at 95-100° at 2 mm.

Reaction of 2-morpholinomethyl pentan-3-one phenylhydrazone with alcoholic hydrogen chloride.

2-Morpholinomethyl pentan-3-one did not give a solid phenylhydrazone on mixing with phenylhydrazine, although reaction readily occurred with evolution of heat.

2-Morpholinomethyl pentan-3-one (10 g.) was dissolved in absolute alcohol (10 c.c.) and phenyl hydrazine (6 g.) added. The solution became warm and was allowed to stand for an hour to ensure completion of phenylhydrazone formation. It was then saturated with dry hydrogen chloride, a vigorous reaction ensuing after about five minutes, with darkening and precipitation of a white solid. After cooling the mixture was diluted with ether and filtered. The gummy precipitate was taken up in hot acetone, and filtered from insoluble material, which proved to be ammonium chloride. From the brown acetone solution colourless crystals deposited on cooling. After recrystallisation from alcohol-ether these were identified as morpholine hydrochloride.

The acetone solution was evaporated, diluted with water and extracted with ether to remove non-basic materials. The ethereal extract on drying and evaporation gave a brown oil which could not be crystallised, but gave Knorr's pyrazoline test on treatment with sulphuric acid. The aqueous layer was basified and the precipitated oil extracted with ether. After drying and removal of ether the residual oil was placed in a vacuum desiccator over sulphuric acid to remove phenylhydrazine. It could not be induced to crystallise, nor would it give crystalline picrate, but it almost certainly contains an indolenine.

ACKNOWLEDGMENT.

One of the authors (R.H.H.) gratefully acknowledges the receipt of a Commonwealth Government Scholarship, which has enabled her to take part in this work.

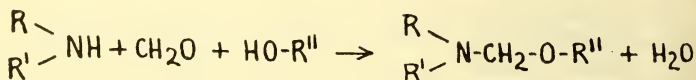
Department of Organic Chemistry,
The University of Sydney.

MORPHOLINOMETHYL ALKYL ETHERS.

By RITA H. HARRADENCE, M.Sc.,
and FRANCIS LIONS, B.Sc., Ph.D.

(Manuscript received, March 22, 1939. Read, April 5, 1939.)

McLeod and Robinson (*J.C.S.*, 1921, 119, 1470) studied the formation of dialkylamino methyl ethers from secondary aliphatic amines, formaldehyde, and primary aliphatic alcohols, and showed that they were readily obtained "by the action of aqueous formaldehyde on the secondary base followed by condensation with the alcohol in presence of an excess of potassium carbonate".



I

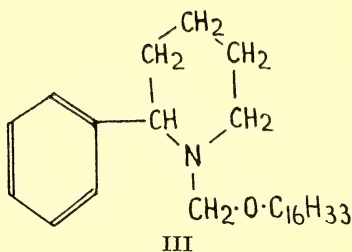
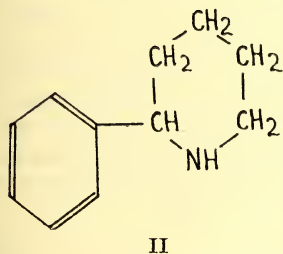
We have now applied this reaction to the secondary heterocyclic base morpholine (I), which has recently been rendered easily accessible, and is probably the cheapest secondary base with aliphatic properties at present available; and have been able to show that (I) readily forms ethers of the type described by McLeod and Robinson.

The general properties and usefulness of the dialkylaminomethyl alkyl ethers have been largely studied and described by McLeod and Robinson (*loc. cit.*) and Robinson and Robinson (*J.C.S.*, 1923, 123, 532). The former authors observed that "in general ethers derived from alcohols of smaller molecular weight are the more readily hydrolysed, derivatives of diethylamine are less stable than those of piperidine, and thio ethers are much more stable than the ethers". The latter authors also observed that the derived quaternary salts of these ethers are remarkably stable, and "resist hydrolysis even in dilute acid solution at 100°".

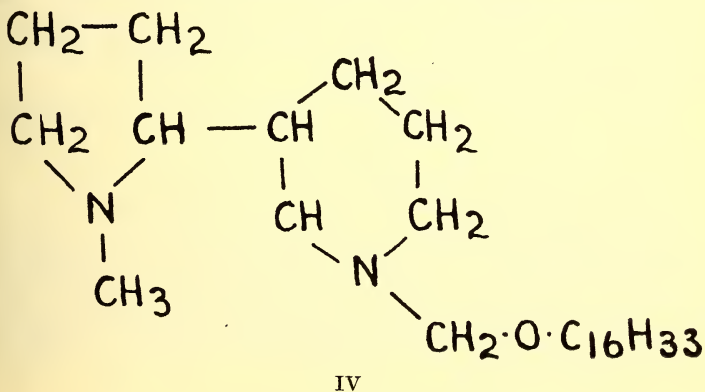
We considered that it would be of interest to ascertain whether the quaternary salts derived from long-chain

alkyl dialkylamino methyl ethers might not have useful properties as emulsifying agents, and in particular, would not be very sensitive to acids; and accordingly prepared some of the cetyl compounds. However, the resistance of these substances to hydrolysis was not nearly so high as might have been anticipated. The derived quaternary salts, however, are more stable and were shown in preliminary tests to be of some value as emulsifying agents. On the other hand, addition of acid does tend to break up such emulsions.

We had also considered that it might be possible to evolve a useful method of applying an alkaloid such as anabasine (II) in insecticidal work, by preparing a water-insoluble derivative (such as the ether III) which would slowly hydrolyse and liberate the base.



As no anabasine was available, hexahydronicotine was prepared and combined with formaldehyde and cetyl alcohol to the ether (IV); but examination of this substance showed that it was very readily hydrolysed. An investigation of thio ethers of this type will be reported later.



EXPERIMENTAL.

Except where otherwise stated the ethers were prepared according to the method of McLeod and Robinson (*J.C.S.*, 1921, 1472), and the equivalents of the bases determined by decomposition with a known excess of N/10 sulphuric acid followed by back titration with N/10 sodium hydroxide solution, using methyl orange as indicator. In the case of the cetyl ethers, addition of N/10 sulphuric acid led to immediate decomposition with precipitation of cetyl alcohol, which made the end point difficult to determine, and thus gave rise to varying results. This difficulty was overcome by extracting the acidified solution with ether before back titration with sodium hydroxide.

Dimorpholino methane.

Equimolecular quantities of morpholine (35 g.) and 40% formaldehyde solution (15 g.) were mixed and the solution saturated with anhydrous potassium carbonate. The reaction was accompanied by evolution of heat. After standing with occasional shaking for several hours the product was extracted with ether, dried over anhydrous potassium carbonate and distilled, being thus obtained as a colourless oil boiling at 139-140°/29 mm.

Found: Equiv. wt.=92; calculated for a diacid base $C_9H_{18}O_2N_2$, equiv. wt.=93.

Morpholinomethyl isopropyl ether.

Isopropyl alcohol (20 g.), morpholine (29 g.) and 40% formaldehyde (28 g.) gave a product, which on fractionation at ordinary pressure gave 7 g. boiling at 180-200°, the remainder boiling at 220-225° and consisting of dimorpholino methane. The fraction 180-200° on re-distillation boiled at 185-195°.

Found: Equiv. wt.=155; calculated for monacid base $C_8H_{17}O_2N$, equiv. wt.=159.

Morpholinomethyl n-butyl ether.

n-Butyl alcohol (18 g.), morpholine (22 g.) and 40% formaldehyde (21 g.) gave on fractionation at ordinary pressure thirty-one grams of an oil boiling at 215-225°/755 mm. An equivalent weight determination gave a value of 160 in place of 173. Refractionation gave 10 g. boiling at 218-222°/760 mm.

Found: Equiv. wt.=162; calculated for a monacid base $C_9H_{19}O_2N$, equiv. wt.=173.

The low value may be due to the presence of some dimorpholino methane, the boiling point of which is not far removed from that of the butyl ether.

Morpholinomethyl cyclohexyl ether.

Cyclohexanol (25 g.), morpholine (22 g.) and 40% formaldehyde solution (21 g.) gave 23 grams of a colourless oil boiling over the range 140-150°/30 mm. An equivalent weight determination gave a value of 153 instead of 199, indicating the presence of some dimorpholino methane. Refractionation gave fractions boiling at 142-145°/29 mm. (equiv. wt. 134) and 145-147°/29 mm. (equiv. wt. 166).

Apparently the dimorpholino methane cannot be entirely separated by fractionation.

Morpholinomethyl β -phenyl ethyl ether.

Morpholine (22 g.), phenyl ethyl alcohol (30 g.) and 40% formaldehyde (21 g.) gave 33 grams of a colourless oil, which, after refractionation, boiled at 184°/25 mm.

Found: Equiv. wt.=223; calculated for $C_{13}H_{19}O_2N$, equiv. wt.=221.

Di(morpholinomethyl) dimethylene ether.

Ethylene glycol (10 g.), morpholine (29 g.) and 40% formaldehyde (28 g.) gave a product which on refractionation under reduced pressure gave 5 grams, b.p. 130-140°/26 mm. (dimorpholino methane), 7 grams b.p. 140-200°/26 mm., and 14 grams b.p. 200-210°/26 mm. The latter fraction on redistillation gave 9 grams, b.p. 205-209°/26 mm.

Found: Equiv. wt.=132; calculated for $C_{12}H_{24}O_4N_2$, equiv. wt.=130.

Di(morpholinomethyl) trimethylene ether.

Trimethylene glycol (13 g.), morpholine (29 g.) and 40% formaldehyde (28 g.) gave a product which was fractionated under reduced pressure. After removal of lower boiling material (up to 190°) the remainder was distilled without a column, giving 24 grams boiling at 190-220°/25 mm. Redistillation gave 20 grams, b.p. 218-221°/27 mm.

Found: Equiv. wt.=138; calculated for $C_{13}H_{26}O_4N_2$, equiv. wt.=137.

Morpholinomethyl cetyl ether.

Morpholine (11 g.) and 40% formaldehyde (10 g.) were mixed under cooling and cetyl alcohol (30 g.) added, followed by K_2CO_3 . The mixture was heated on the water bath with frequent shaking for one hour. After standing for several hours it was extracted with ether, dried with anhydrous potassium carbonate and distilled in high vacuum. Some cetyl alcohol (b.p. $160-190^\circ/1$ mm.) was recovered and 25 grams (b.p. $195-205^\circ/1$ mm.) were obtained. Redistillation gave 16 grams boiling at $198-202^\circ/1$ mm.

Found: Equiv. wt.=344; calculated for $C_{21}H_{43}O_2N$, equiv. wt.=341.

The ether was gradually hydrolysed in the presence of water, but on the addition of a slight trace of acid instantaneous separation of cetyl alcohol took place.

On allowing to stand with an equivalent quantity of methyl iodide the methiodide gradually crystallised out. Recrystallised from alcohol it formed pale yellow waxy needles. On heating it became transparent at 100° , then opaque, and finally melted at 160° .

Found: I=26.6%; calculated for $C_{22}H_{46}O_2NI$, I=26.3%.

The methosulphate was formed similarly, reaction occurring with evolution of heat. The product on recrystallisation from alcohol formed colourless waxy crystals. These became sticky when pressed on a porous tile and a melting point could not be obtained.

Both these quaternary salts possessed emulsifying properties, but the emulsions were not stable.

Piperidinomethyl cetyl ether.

Piperidine (14 g.), 40% formaldehyde (13 g.), and cetyl alcohol (40 g.), treated as described for the morpholino ether, gave an oil which was fractionated in high vacuum. The following fractions were collected (1) up to $110^\circ/3$ mm., 6 grams, (2) up to $200^\circ/3$ mm., 13 grams consisting of cetyl alcohol, (3) $200-235^\circ/3-4$ mm., 30 grams. Fraction (3) on refractionation gave some cetyl alcohol, then 17 grams boiling at $204-210^\circ/2.2$ mm., and the latter when redistilled gave 11 grams boiling over the range $200-202^\circ/1.5$ mm.

Found: Equiv. wt.=344; calculated for $C_{22}H_{45}ON$, equiv. wt.=339.

On treating with an equimolecular quantity of methyl iodide and allowing to stand the methiodide gradually crystallised out. Recrystallised from alcohol it formed pale yellow crystals m.p. 124°.

Found: I=26.0%; calculated for $C_{23}H_{48}ONI$, I=26.4%.

Diethylaminomethyl cetyl ether.

Diethylamine (12 g.), 40% formaldehyde (13 g.) and cetyl alcohol (40 g.) were reacted as described for the morpholino compound. The resulting oil on fractionation gave unchanged cetyl alcohol, then 24 grams boiling at 184-190°/2 mm. Redistillation gave 17 grams boiling at 185-188°/2 mm. This gave an equivalent weight of 347 instead of 327 as calculated for $C_{21}H_{45}ON$, indicating the presence of cetyl alcohol. On refractionation it boiled at 183-185°/1.7 mm.

Found: Equiv. wt.=338; calculated for $C_{21}H_{45}ON$, equiv. wt.=327.

The high value indicates that cetyl alcohol is still present, it being difficult to effect complete separation because of the proximity of the boiling points.

The methiodide on recrystallisation from alcohol-ether gave pale yellow needles m.p. 105°.

Found: I=27.3%; calculated for $C_{22}H_{48}ONI$, I=27.1%.

Hexahydronicotiny l cetyl ether.

Hexahydronicotine (10 g.), 40% formaldehyde (4.5 g.) and cetyl alcohol (14 g.) were reacted according to the instructions for the morpholino compound. The product on distillation in high vacuum gave unchanged cetyl alcohol and 10 grams boiling at 240-260°/2-3 mm. On redistillation decomposition largely occurred giving much cetyl alcohol and 3.5 grams of a viscous oil boiling at 250-255°/2 mm.

Found: Equiv. wt.=206; calculated for $C_{27}H_{54}ON_2$, equiv. wt.=211.

The product reacted readily with methyl iodide but the gummy methiodide produced could not be crystallised. It also gave a picrate which could not be crystallised. It was noticed that on standing several days cetyl alcohol began to separate from the oil.

ACKNOWLEDGMENT.

One of the authors (R.H.H.) gratefully acknowledges the receipt of a Commonwealth Government Research Scholarship which has enabled her to take part in this work.

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THE MESOZOIC STRATIGRAPHY OF THE MERRIWA-MURRURUNDI DISTRICT AND SOUTH-EASTERN LIVERPOOL PLAINS.

By J. A. DULHUNTY, B.Sc.

(With Plate I and two text-figures.)

(Manuscript received, April 3, 1939. Read, May 3, 1939.)

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INTRODUCTION.

The area described in this paper includes the country situated immediately to the north and south of the eastern portion of the Liverpool Range. It extends to the boundaries of two other districts in which the Mesozoic stratigraphy has been worked out, namely the Goulburn River district to the south-west and the Gunnedah-Coonabarabran district to the north-west.

In the Goulburn River district the presence of Jurassic sediments outcropping along the southern side of the Liverpool Range was first recognised between Merriwa and Cassilis.⁽¹⁾ It was found possible to make a distinction between Jurassic and Triassic rocks by tracing a bed of shales, termed the Comiala Series, to the vicinity of the Talbragar "Fish-Beds" near Ulan (see ⁽²⁾ and references therein). At this point plant and fish fossils of Jurassic age occur at the base of a sandstone series (the Munmurra Beds) which overlies the Comiala shales, while another

sandstone series (the Wollar Sandstone), which underlies the shales, is continuous with the Triassic beds overlying Kamilaroi sediments to the south-east. The Comiala Series has been taken as a line of demarcation between Triassic and Jurassic, giving the following sequence in the Mesozoic strata and underlying Kamilaroi rocks of the Goulburn River district :

Jurassic ..	Munmurra Beds.	Porous sandstone with basal conglomerates in places.
?	Comiala Series.	Mainly shales with some "red beds" and tuffaceous bands.
Triassic ..	Wollar Sandstone.	Sandstone and fine conglomerates.
Kamilaroi ..	Upper Coal Measures.	Coal seams, shales, white cherts and tuffaceous sandstone bands.

The Mesozoic strata of the Gunnedah-Coonabarabran area, extending south to the Tertiary basalts of the Liverpool Range and occupying the western and north-western portions of the Liverpool Plains, have been mapped and described by Mr. E. J. Kenny⁽³⁾ in connection with the work of the Geological Survey of New South Wales on the intake beds of the Great Artesian Basin. Kamilaroi coal measures dipping to the west outcrop between Curlewis and Gunnedah. These are followed in vertical sequence by lower Mesozoic strata, which have been subdivided into basal sandstones, grits, and conglomerates known as the Digby Beds, and an overlying series of sandstones, sandy shales, and clay shales which have been called the Napperby Beds.

Towards the centre of the area there occur contemporaneous lava flows, which have been termed the Garrawilla Series, overlying the Napperby Beds. The interbedded lavas are followed in turn by the Purlawaugh Beds, which consist of shaly sandstones and shales, and are characterised

by the presence of hæmatitic ironstone bands or "red beds". These beds are overlain by thick deposits of Jurassic sandstone, known as the Pilliga Beds, which form the main aquifer of the Great Artesian Basin. The following table illustrates the stratigraphical sequence in the Gunnedah-Coonabarabran district⁽³⁾ :

Jurassic ..	Pilliga Beds .. Purlawaugh Beds ..	Coarse porous sandstone. Shaly sandstones, shales and "red beds".
Lower Mesozoic	Garrawilla Series ..	Contemporaneous lava flows.
	Napperby Beds ..	Mainly sandy shales.
	Digby Beds ..	Mainly conglomerates.
Kamilaroi ..	Gunnedah - Curlewis Coal Measures ..	Coal seams, clay shales, conglomerates and sand- stones.

The absence of fossil evidence in the Digby and Napperby Beds and Garrawilla Series has made it impossible to draw a definite line of subdivision between Jurassic and Triassic strata, but it has been suggested by E. J. Kenny and A. C. Lloyd⁽⁴⁾ that the sandstones and conglomerates in the basal portion of the Digby Beds may be of Triassic age.

In the present paper the Mesozoic strata are described in the Merriwa-Murrurundi district which lies to the south of the eastern end of the Liverpool Range, and also the strata in the south-eastern portion of the Liverpool Plains, situated to the north of the range. The latter area extends as far north as a line through Quirindi and Caroona, while it is terminated to the east by the New England Highway between Murrurundi and Quirindi, and on the western side the work was carried across the Mooki River for about ten miles to connect with the country already mapped by E. J. Kenny. The geological mapping of these two areas was undertaken with the object of determining the south-eastern distribution of Jurassic sediments, and also to carry the distinction between Triassic and Jurassic beds

round the eastern end of the Liverpool Range into the Mesozoic strata of the Gunnedah, Coonabarabran and Binnaway districts, and adjoining areas.

STRATIGRAPHY OF THE MERRIWA-MURRURUNDI DISTRICT AND SOUTH-EASTERN LIVERPOOL PLAINS.

Triassic Beds.

In the Triassic rocks of the Goulburn River district, to the south-west of Merriwa, there is a considerable difference in the lithology of the upper and lower portions of the series. The lower portion, which is about 400 feet in thickness, is decidedly conglomeratic, being made up of coarse-grained sandstone packed with small rounded pebbles, mainly white quartz with a limited amount of red and black jasper. The upper portion, some 250 feet in thickness, is a homogeneous medium-grained sandstone. The change in lithology is fairly sharp and divides the series into two distinct types. In the Merriwa-Murrurundi district, the distinction between the fine-grained upper and coarse-grained lower portions of the Triassic is well marked, especially along the western scarp of the Middle Hunter Valley and Kingdon Ponds Valley, where it was observed by H. G. Raggatt, who drew the writer's attention to the feature. Certain changes take place within the two portions of the series as it passes to the east and north-east from Merriwa to the Kingdon Ponds Valley. The lower beds become coarser and assume the nature of a true conglomerate, with pebbles up to five and six inches in diameter consisting largely of black, red, and greenish-blue jasper, as well as a considerable amount of white quartz. The upper beds of the Triassic do not vary in grainsize as they pass to the east, but interbedded lenses of sandy shale commence to make their appearance towards the top of the formation between Merriwa and Bunnan, and become quite a pronounced feature in the section through the Triassic at Owen's Gap (Fig. 1) between Bunnan and Scone. The outcrop of Triassic strata is illustrated in the accompanying geological map (Plate I).

From Owen's Gap the outcrop of the Triassic beds runs north to Murrurundi (mapped by Geol. Surv. N.S.W., 1932). It can be followed continuously along the margin of the Tertiary basalt flows which extend down from the Liverpool Range, although it is largely covered by basalt between Wingen and Blandford. At Murrurundi it forms low cliffs which stand out prominently on the hillside about one mile

from the township on its southern side. At this point the lower beds of the Triassic still retain their marked conglomeratic nature, but appear to have become considerably reduced in thickness. The upper fine-grained portion of the Triassic is present at Murrurundi but it is much thinner than at Owen's Gap and in the vicinity of Dart Brook. The strata have been much disturbed by faulting in the vicinity of the gap about two miles to the west of Murrurundi, where the New England Highway crosses the Main Divide, and the ridge at this point is largely covered by basalt. On the western side of the Divide, between Ardglan and Willow Tree, Triassic rocks again make their appearance from beneath the Tertiary basalt flows, and their outcrop continues to run north-west along the south-western side of Borambil Creek to the vicinity of Quirindi. The Triassic beds as a whole decrease in thickness as they pass to the north-west, and the upper fine-grained portion cuts out completely about three miles north-west of Willow Tree. The conglomerates of the lower portion continue till they reach a point about five miles west of Quirindi, where they become submerged in the black soil alluvium of the Liverpool Plains. The Plains continue to the north-west for about nine miles to Caroona on the Mooki River, where the Triassic again outcrops, but the lower coarse portion is alone represented.

The thinning of the Triassic beds to the east and north, and the gradual lateral passage of the lower portion into conglomerates, strongly suggest that the beds outcropping between Scone and Quirindi represent shoreline facies of the Triassic sediments. It is evident from the contortion of the beds that considerable post-Triassic faulting has occurred between Murrurundi and Quirindi, and that the present eastern margin of the Triassic has been determined by this faulting, but it is probable that the Triassic sea did not extend much further to the east than is indicated by the present position of its sediments. The cutting out of the upper portion without the development of coarse-grained phases suggests a receding shoreline accompanied by quiet conditions of deposition towards the close of Triassic sedimentation in this part of the State.

The Comiala Series and the Demarcation of Triassic from Jurassic.

In the Goulburn River district between Merriwa and Cassilis the Comiala Series consists mainly of clay shales,

mudstones and shaly sandstones. There is a marked tendency towards the development of tuffaceous bands near the middle of the series, forming a natural subdivision into upper and lower portions. This forms an important feature in correlating the Comiala Series with the Mesozoic beds of adjoining areas, as will be pointed out later in this paper. A limited quantity of hæmatitic ironstone bands, known as "red beds", occurs in the Comiala Series. These beds possess a deep brownish-red colour, giving a brilliant red streak, and may be somewhat sandy or argillaceous. They are typical of the Jurassic sediments in the Dunedoo, Coonabarabran, and Gunnedah districts, and provide valuable indicators when tracing discontinuous outcrops of a series which contains them. (These beds should not be confused with the chocolate shales of the Triassic Narrabeen beds, which are quite different lithologically.) Up till the present the Comiala Series has been taken as a line of demarcation between Triassic and Jurassic strata, the age of the series itself being uncertain. During recent work, however, the writer has found Jurassic plant fossil assemblages at the base of the Comiala beds. The fossil evidence, together with the presence of the "red beds", is considered sufficient to establish the Jurassic age of the Comiala Series. This being so, the horizon represented by the base of the series may be taken as the top of Triassic strata and the base of Jurassic sediments in those areas into which the horizon can be traced.

At Merriwa the thickness of the Comiala beds is about 30 feet, the tuffaceous beds and upper portion of the series having cut out. As the horizon passes to the east, clay-shales occur only as large lenticular masses, but the presence of the lower portion of the series is well marked by "red beds" and some sandy shales. Between Gungal Creek and Guan Creek (see Plate I) the lower Comiala beds are largely covered by Tertiary basalt, but towards Owen's Gap they outcrop at the edge of the flows, where they are well characterised by "red beds", and commence to increase in thickness, although soft clayshales are limited in quantity. At the highest point on the main road where it passes through Owen's Gap there is a thin veneer of Comiala sediments, about thirty feet in thickness, lying on the rather shaly beds of the upper portion of the Triassic series. The Jurassic beds dip to the west at about 3°, and occupy a dip-slope on the western side of the Gap. This is illustrated in the following section (Fig. 1) through

a high basalt ridge on the southern side of the road, where the Jurassic beds amount to about 200 feet in thickness, having been protected from erosion by the basalt flow.

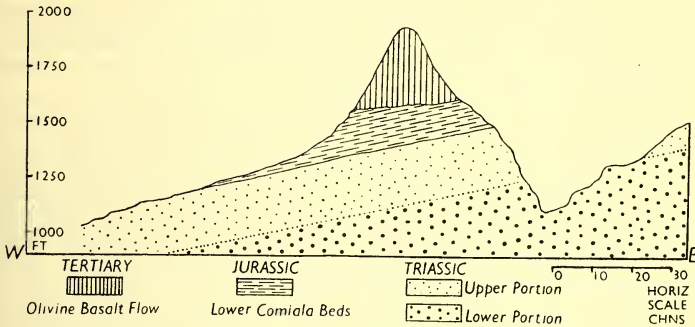


Fig. 1.—Geological Section at the southern side of Owen's Gap.

From Owen's Gap the outcrop of the Comiala beds passes to the north round the heads of Dart Brook and Middle Brook, and then becomes covered by Tertiary basalt until it again emerges on the eastern side of the Main Dividing Range, one mile to the south-west of Murrurundi. At this point the outcrop of the beds is covered to a large extent by talus from the high basalt ridges, but their presence is indicated by some ferruginous shales and "red beds". The Jurassic age of the Comiala Series is confirmed at Murrurundi by the presence of a soft ferruginous rock, blue-grey to brown in colour, which is crowded with fragmentary plant remains and some reasonably well preserved plants which constitute a typical Jurassic assemblage. The material appears to occur near the base of the series, and contains *Coniopteris hymenophylloides*, *Cladophlebis australis* and *Tæniopteris daintrei*. Dr. A. B. Walkom, who identified the fossils, considers that they constitute an assemblage similar to that found in Jurassic sediments at Bexhill, near Lismore,⁽⁵⁾ and Beaudesert,⁽⁶⁾ about 50 miles south of Brisbane, and also that the rock material from Murrurundi closely resembles the material from the above localities.

The possibility of Jurassic sediments outcropping at the margin of the Tertiary basalt flows in the vicinity of Owen's Gap and Dart Brook was first suggested by H. G. Raggatt, who found plant fossils in Dart Brook Valley closely resembling Jurassic types. He exhibited a section

illustrating the probable occurrence of Jurassic beds at Owen's Gap, and pointed out the significance of the fossils, at a Geological Section meeting of the Royal Society of New South Wales in 1932.⁽⁷⁾ The work described in this paper confirms Mr. Raggatt's suggestion, and it is evident that the horizon from which he obtained the fossils is near the base of the lower Comiala beds and equivalent to the fossiliferous beds at Murrurundi.

On the western side of the Main Divide the first outcrop of Comiala sediments is about two miles to the south-west of Willow Tree, on the ridge between Borambil and Warrah Creeks. Fairly extensive outcrops of the lower portion of the Comiala beds occur along dip-slopes on the eastern side of Warrah Creek Valley, and extend north-west to a point about six miles west of Quirindi, where they become covered by alluvium. From this point the lower portion of the series can be followed across the plains by means of discontinuous outcrops forming "islands" in the alluvium (see Plate I) to Caroonna on the Mooki River, where the beds can be seen in contact with the Triassic conglomerates. At Caroonna Railway Station there is a bed of soft brownish-grey ferruginous material occurring at the base of the Comiala beds, which resembles very closely the fossiliferous beds at Murrurundi. It contains much fragmentary plant material, among which *Cladophlebis australis* has been identified. This occurrence and the one at Murrurundi substantiate the fact that the base of the Comiala Series may be taken as the line of subdivision between Jurassic and Triassic strata. The lower Comiala beds extend to the west of Caroonna for about three miles along the Spring Ridge road, where the presence of "red beds" has produced a typical brownish-red gravel on the surface. This lower portion of the Comiala Series eventually passes into the Napperby beds of the Gunnedah-Coonabarabran district.

The Pilliga Sandstone, Purlawaugh or Upper Comiala Beds and Garrawilla Series.

A series of contemporaneous lavas equivalent to the Garrawilla Series outcrops in the south-eastern Liverpool Plains and occupies a position immediately overlying the lower Comiala beds. The outcrop passes down the western side of Warrah Creek Valley, and then across through Pine Ridge to Caroonna (see Plate I), where it swings more to the west, passes through Spring Ridge, and thence becomes continuous with the Garrawilla Series to the north-west.

The lavas are overlain by a formation consisting of sandy ferruginous shales and "red beds", which is equivalent to the Purlawaugh Beds of the Gunnedah-Coonabarabran district. The outcrop of these beds can be followed from the edge of the Liverpool Range basalt across the plains to Caroon and Spring Ridge (see Plate I). The Purlawaugh Beds are followed in vertical sequence by beds of massive sandstone which become the Pilliga Sandstone to the west of Spring Ridge.

It is evident from their stratigraphical position and lithological types that the Purlawaugh Beds represent the upper portion of the Comiala Series. It follows that the Garrawilla lavas, which become thinner as they pass to the south, actually split the Comiala Series, but the thinning of the flows causes them to cut out before reaching the Goulburn River district, where the lavas are definitely absent from the Jurassic sequence, but their horizon is indicated by the tuffaceous bands which occur near the middle of the series. In the Merriwa-Murrurundi district thick flows of Tertiary basalt cover those areas in which the Garrawilla Series may be expected to outcrop.

The Jurassic Munmurra Sandstone of the Goulburn River district overlaps the upper portion of the Comiala Series at Merriwa as it passes to the east, and does not outcrop from beneath the Tertiary basalts in the Merriwa-Murrurundi area any further east than Gungal Creek. On the northern side of the Liverpool Range the same sandstone beds appear on the western side of Warrah Ridge, overlying the Purlawaugh Beds. Its outcrop is rather indefinite, but becomes more pronounced as it passes to the north-west. In the vicinity of Pine Ridge and Spring Ridge it forms typical Jurassic sandstone country, and to the west it is continuous with the Pilliga Beds.

The above results indicate that the Purlawaugh Beds overlap the Garrawilla Series in the vicinity of the Liverpool Range as they pass to the south-east, and that the Purlawaugh Beds are in turn overlapped by the sandstone of the Pilliga Beds in the Merriwa-Murrurundi district. These features are illustrated in the accompanying geological section, Fig. 2. It is possible that an anticlinal structure may occur under the basalt of the Liverpool Range, which would mean that the thickness of the Pilliga sandstone is less than indicated in the section.

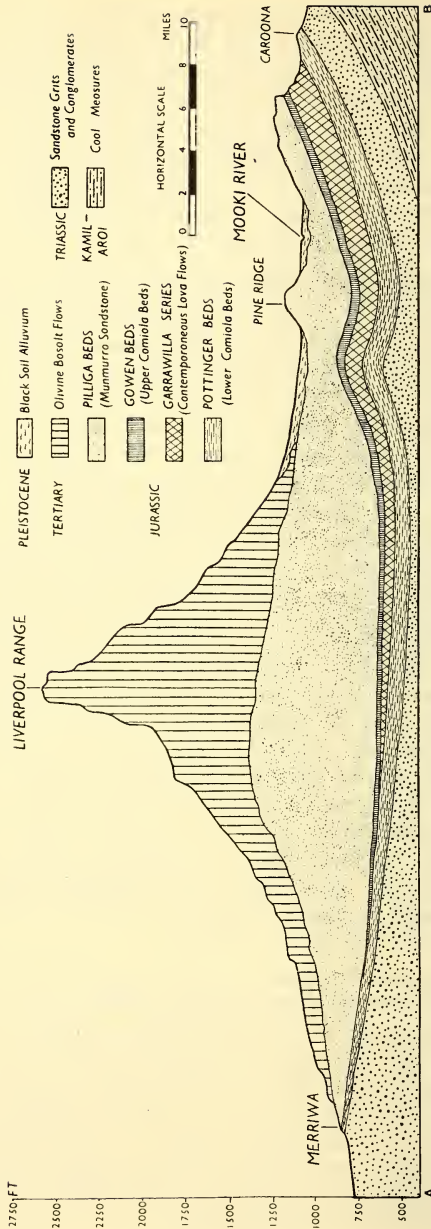


Fig. 2.—Geological Section (along A-B, Plate I) from Merriwa to Caroona.





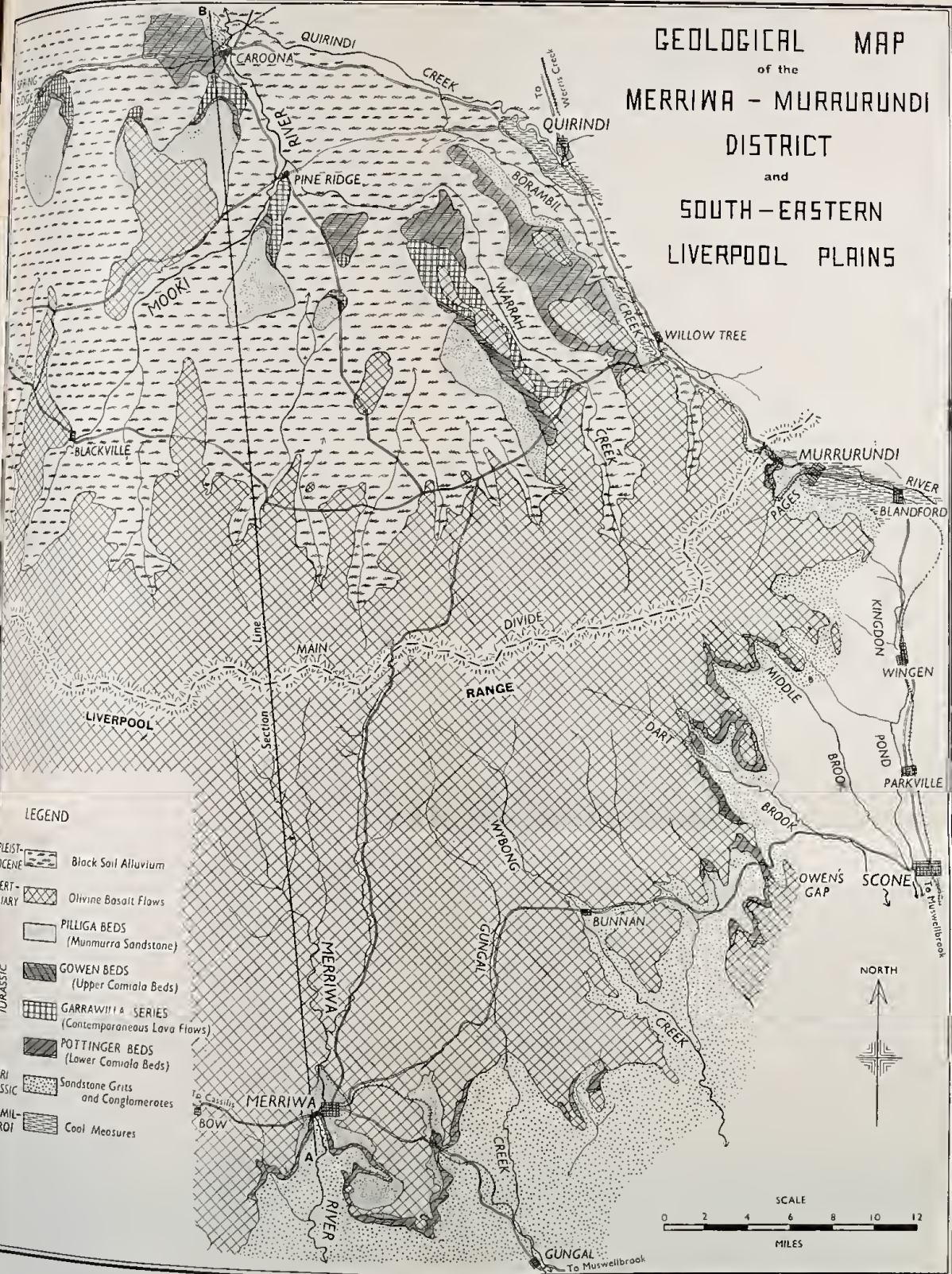
GEOLOGICAL MAP

of the

MERRIWA - MURRURUNDI DISTRICT

and

SOUTH-EASTERN LIVERPOOL PLAINS



LEGEND

- PLEISTOCENE Black Soil Alluvium
- TERTIARY Olivine Basalt Flows
- PILLIGA BEDS (Munmurra Sandstone)
- JURASSIC GOWEN BEDS (Upper Comiala Beds)
- GARRAWILLA SERIES (Contemporaneous Lava Flows)
- POTTINGER BEDS (Lower Comiala Beds)
- TRIASSIC Sandstone Grits and Conglomerates
- KAMIL-AROI Cool Measures



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TABLE OF CORRELATION OF THE MESOZOIC STRATA IN THE MERRIWA-GUNNEDAH REGION.

System.	Proposed Subdivisions.	Former Subdivisions in Individual Areas.			
		Goulburn River District.	Merriwa-Murrurundi District.	South-Eastern Liverpool Plains.	Gunnedah-Coonabarabran District. (3)
Jurassic	Pilliga Beds . .	Mummurra Sandstone.	Mummurra Sandstone. (No outcrops.)	Pilliga Beds.	Pilliga Beds.
	Gowen Beds . .	Upper Comiala Series.	—	Purlawaugh Beds.	Purlawaugh Beds.
	Garrawilla Series	—	—	Garrawilla Series.	Garrawilla Series.
	Pottinger Beds	Lower Comiala Series.	Lower Comiala Series.	Napperby Beds.	Napperby Beds.
	Upper Portion	Wollar Sandstone.	Wollar Sandstone.	—	—
Triassic	Lower Portion	Lower	Lower	Digby Beds.	Digby Beds.

CORRELATION WITH ADJOINING AREAS, AND INTRODUCTION OF UNIFORM SYSTEM OF NOMENCLATURE.

In view of the fact that it is now possible to correlate the Mesozoic strata of the districts on the southern side of the Liverpool Range with those to the north and west, it has been decided, after consultation with Mr. E. J. Kenny, that uniform names should be adopted for the principal subdivisions of the Mesozoic which have been recognised over large areas. The terms decided upon are shown in the following table under the heading of "Proposed Subdivisions", and it is intended that they shall be used, rather than local place names, in referring to the various strata throughout the different districts in which they occur. No special names have been given to the Triassic beds, as they have not yet been correlated in detail with the Triassic sequence overlying the Kamilaroi sediments to the south, and consequently their stratigraphical position in relation to Triassic sedimentation is still uncertain. The terms "Upper Portion" and "Lower Portion" used in the accompanying table refer to the upper and lower portions of that particular stage of the Triassic which occurs in the districts concerned, and have no reference to upper and lower Triassic age.

In conclusion, the writer wishes to acknowledge assistance given by members of the Geological Survey of New South Wales in making available detailed information concerning adjoining areas, and also helpful discussion with Professor W. R. Browne.

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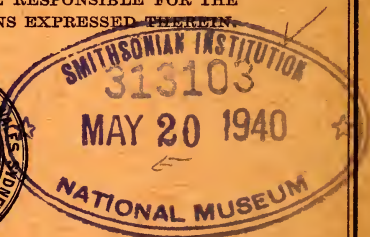
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PIONEERS OF BRITISH GEOLOGY.¹

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INTRODUCTION.

The latter part of the eighteenth century was a period that saw immense progress in physical and natural science. Especially in France there was very great intellectual activity, culminating in the production of the famous encyclopædia, in which all the principal scientists of the day took part. Astronomy in particular was making great progress, assisted by the advances in mathematics and physics. The work of Laplace and his coadjutors formulated a theory of the motions of the planets and their satellites and of the physical history of the solar system that was founded on well established scientific principles and obtained general acceptance. The hypothesis was at once simple and all-embracing. A primary gaseous nebula had filled the space now occupied by the sun and planets. This nebula was in rotation and at the same time suffered gradual condensation. As motion increased the

¹ Clarke Memorial Lecture delivered to the Royal Society of New South Wales, April 28th, 1939.

planets were thrown off in succession, one following another, and they also were nebulous rotating masses. Condensation was attended by cooling and in course of time the outer planets passed into the liquid condition; subsequently a solid crust formed, enclosing a still liquid centre. Through these stages the earth had gradually passed till it attained its present state. The temperature of the sun was still very high, but in course of time it too would cool down to the liquid state and finally solidify. There seemed no difficulty in believing that the earth had passed from a gaseous condition to the liquid before assuming its present state. The solid crust enclosed a nucleus that was intensely hot and presumably liquid, and the earth as a whole was cooling down slowly but inevitably. It was known that the earth's interior had a high density and probably contained a large proportion of metals.

In the natural sciences, also, great advances had been made. Linnæus and his school had produced a working classification of plants and animals, which, though it is no longer employed, afforded a ready means of arranging and determining the species that were then known to naturalists. The principles of his classification were purely artificial, but many of the natural families and genera were clearly recognised. Even more significant of future developments was the work of Lamarck, who was Professor of Natural History in the Museum in Paris. He enunciated that the various genera of the animal and vegetable kingdoms had originated by development and differentiation from ancestral forms. The cause of differentiation was adaptation to environment together with the inheritance of acquired characters. In consequence he was an opponent of the idea then current that genera and species were the result of special creations. Lamarck's theories, though superseded in the main by those of Wallace and Darwin, who ascribe differentiation to the struggle for existence and the survival of the fittest, still have supporters among modern naturalists and are not entirely discarded. They are specially important, however, as appealing to the operation of natural causes, and emphasising the effects of minute changes continued over long periods of time.

The growing interest in the variety and beauty of plants and animals led to an intense activity in forming collections. Travellers visited the most distant parts of the world and brought home great stores of preserved material for study by naturalists. Many rich men employed professional

collectors to enrich their cabinets with specimens from distant lands. Private museums were numerous and, some of them, famous, and the description of newly discovered species proceeded at a great rate. One of the most famous of these naturalists was Sir Joseph Banks, who visited Australia with Captain Cook and on his return was a most munificent patron of natural science and was elected President of the Royal Society of London. His collections are now in the British Museum.

GEOGNOSEY AND GEOLOGY.

The study of geology was also being prosecuted with great enthusiasm. The name given to the science at that time was Geognosy (knowledge of the earth) and its devotees might be described as 'geognostics'. It was their object to ascertain, describe, and classify all the materials encountered in the earth's crust. Some of them formed enormous collections, of which they were intensely proud, and a vast descriptive terminology was invented to enable them to present the results of their researches in literary form. For a variety of reasons not much of their work has survived. The advance of more scientific methods of investigation has swept away the results of their investigations, as many of their classifications were based on purely superficial characters and had no scientific basis. Of their industry and enthusiasm, however, there could be no doubt. In England this school was represented by Woodward, a London physician who had a wonderful cabinet of specimens, and in whose memory the Woodwardian Museum of Cambridge was subsequently named.

The geognostics were much interested in minerals, as might be anticipated from their variety, beauty, and economic value. Most of the common ores and spars were well known to them. They had an elaborate descriptive terminology for their colours, lustres, hardness, specific gravity, fracture, odour, feel, and other superficial characters, but many minerals eluded their diagnosis and they had great difficulties with the fine grained and compact aggregates: hence their determination of rocks, especially the finer crystalline varieties, was often very unsatisfactory. Moreover, as systematic and analytical chemistry was still in its infancy, they often placed together minerals of very different composition, and, as crystallography had still to be erected on a firm basis, their

description of the crystalline forms of minerals lacked scientific foundation. The principal forms of the commonest minerals, however, such as pyrites, calcite, quartz, garnet, and fluorspar, were well known to them, and are often represented by accurate drawings in their memoirs. By the term 'fossils' they designated everything inorganic found in the earth's crust, but subsequently the name has become restricted to the remains of animals and plants enclosed in the rocks. In organic fossils the geognostics took comparatively little interest; in fact they seemed to be rather disconcerted by their presence, and few serious efforts were made to determine their exact nature and significance. It was well known for example, that the Chalk, the London Clay, and the Mountain Limestone contained many remains of fossil animals, and that there were well preserved plant remains in the Coal Measures. Many of these were figured and described and their affinities to living animals and plants were discussed, but there was little apprehension of their value as evidence of the former history of the earth and the stages through which it has attained its present state.

The geognostics also were great travellers and investigated every part of Europe and many other countries especially in search of minerals and rocks. They even appreciated the value of maps showing the distribution of various types of rock such as chalk, clay, mudstone, granite, and porphyry. In Scotland they were well acquainted with the geognosy of all the principal districts where there were good roads, and even with some of the outlying islands and highland mountains. Sir Joseph Banks, for example, was the discoverer of the famous columnar rocks of the island of Staffa, off the coast of Mull. These rocks puzzled the geognostics exceedingly, and in the early years of the nineteenth century they were visited by geologists from many countries and were described in a special volume by the famous Frenchman, Faujas de St. Fond.

In the beginning of the nineteenth century Geognosy occupied the field now assigned to Geology. The term geology was first used by De Luc (himself a convinced geognostic) in 1826, and gradually replaced the older designation as geognosy fell into disrepute. The science of geology was founded on the ruins of geognosy during the first thirty years of the nineteenth century; what was good in the older system was incorporated in the new; what was worthless was rejected. As might be expected

there was much bitter controversy during the period of transition. It is to be noted also that British geologists played a very important part in establishing the new science. If we wish to understand the controversies of that time, and the rapid and fundamental advances that were made by the new school of thought, it is necessary to examine somewhat briefly the principal tenets of the geognostic creed.

It is not to be supposed, of course, that all the geognostics were in agreement on all points. There were differences of opinion, no doubt, and as time went on these became more emphatic as the more intelligent members of the cult changed their minds in accordance with the increasing weight of evidence against their previous beliefs. One of the most interesting features of the history of geology at this stage is the manner in which the new doctrines gradually made their way and their effect upon the minds of prominent geologists. It is true, nevertheless, that the geognostic doctrines continued to be held with great tenacity, and, in fact, hardly any geologist who in early life had been a geognostic ever completely renounced his previous views. An example may be cited in Dr. John MacCulloch, who lived through the transition period and died in 1835; he was never completely convinced that in all respects the new doctrines were superior to the old.

THE WERNERIANS.

About the close of the eighteenth century the centre of geognostic teaching was Friberg in Saxony, where Professor Abraham Gottlob Werner was professor in the Bergakademie. He died in 1817 and for forty years he had been the leader of German thought in geology, and one of the most famous scientists in Europe. As a teacher he was an eminent success and the fame of his lectures attracted students from all parts of Europe. Of these one of the most distinguished was Robert Jameson, afterwards Professor of Natural History in Edinburgh University. Werner's lectures were very comprehensive and treated of the whole of mineralogy, geology, and physical geography as they were understood at that time. He was a man of charming personality and his students were devoted to him; his personal influence must have been very great, as men of the highest intellectual capacity, like von Buch and Humboldt, not only accepted the theories he taught

but remained profoundly attached to him till the close of his life. He taught his subject in a very philosophic manner, showing the application of 'earth-knowledge' to many problems of social and economic importance, to history, travel, industry, and all the varied field of human experience. Unwilling to commit his views to paper, he published comparatively few memoirs, and gave no consistent or complete exposition of his doctrines; we are indebted for most of our knowledge of them to the accounts published by his pupils in Germany, France, and England. The system he promulgated has become known as Wernerianism, and embraced the dominant orthodox views on the science of geognosy up to about the end of the second decade of the nineteenth century.

In his theory of the earth Werner followed the cosmogony of the astronomers of his time. The earth cooled slowly from an incandescent state, and after the solid crust had formed, and in some measure cooled, the watery vapours of the atmosphere began to be precipitated and formed a universal primeval ocean. From this hot ocean, impregnated with siliceous and saline matters, the first rocks to be deposited were crystalline gneissés and schists, with granite and other 'primary' rocks. As cooling progressed another series of deposits was laid down—the 'transition' rocks and the 'floetz' series, which were sediments such as greywacke, sandstone, slate, shale, and limestone. In this series were included beds of trap, the floetz-trap. The next group to be deposited by the ocean were the secondary rocks such as chalk, lias, oolite, and many clays and sandstones. As conditions more closely approached those that prevail at the present day the various superficial deposits such as gravel, sand, mud, and shelly beds were finally deposited. Everywhere the action of sedimentation in water was strongly insisted on, and hence his hypothesis has obtained the name of Neptunism.

Werner, also, was strongly attracted to the study of veins, as he and his family had long been connected with mining. Practically all veins, he pronounced, were due to secretion from the adjacent rocks by the action of water, though some might possibly be due to fissures which had been filled with sediment that had been deposited in open cracks by the waters of the sea.

THE VULCANISTS.

The existence of extinct volcanoes in various parts of Europe had already been established on convincing evidence, principally by the French geologists Guettard, Desmarest, and Montlosier. They had shown that in Auvergne, in Central France, there were volcanoes with craters perfectly preserved, and with lava streams that had proceeded from these craters. The slaggy tops of the lavas and the beds of volcanic cinders were exactly similar to those which were displayed on Vesuvius and other active volcanoes. The characteristic lava-rock was a fine-grained, dark, compact mass with sporadic larger crystals—the basalt of the ancient writers. These men were known as Vulcanists, and they insisted that the dark floetz-trap so common in parts of Scotland, Germany, and France, with occasional cavities lined with crystals, and with frequent prismatic jointing, was simply an ancient lava, and not a strange sediment deposited from water. In pursuit of evidence in this problem many geologists visited Staffa and the Giant's Causeway in the north of Ireland, and most of them, like Faujas de St. Fond and Ami Boué, returned convinced that the Irish and Scottish basalts with beautiful columnar jointing were true volcanic rocks; but the British Wernerians, Jameson, Kirwan, and De Luc refused assent. Gradually, however, the vulcanists prevailed, especially after Humboldt's description of Central American and Mexican volcanoes. Some of them, however, went so far as to assert that the elevation of mountains was due to the upward force of volcanic masses gradually raising the strata. In its cruder form this hypothesis no longer holds the field, though there are still geologists who hold that the granites and granitic gneisses often found in the cores of mountain ranges played an effective part in elevation of the strata.

This was a very great step in advance in the interpretation of Earth-history. We may recall that in New Zealand, especially near Auckland, there are many extinct volcanoes with craters and lavas so perfectly preserved that no one has any difficulty in realising their nature. Similar volcanic structures exist in South Australia. But in New South Wales, among the older rocks, there are black basalts so perfectly interstratified with sandstones and shales that it is easy to believe that they are a connected series of deposits. Outlying masses of basalt occur capping some of the highest of the Blue Mountains. No craters are seen

from which they might have proceeded, and it was by no means an easy matter to arrive at a correct interpretation of their origin and history. Enormous masses of ancient volcanic rocks occur in the Palæozoic strata of New South Wales, and the recognition of the importance of volcanic action in the stratigraphical sequence was a very important discovery. Modern methods of investigation make the identification of volcanic rocks simple and certain, but the early vulcanists had no such assistance and deserve great credit for their acumen. In the Sydney district, also, there are numerous dykes now known to be of volcanic origin and to have been injected into fissures from volcanic magmas situated far below the surface.

THE NATURE OF FOSSILS.

For many years there had been great controversies regarding the nature of fossils, but it was now generally recognised that they were the remains of plants and animals that had died in or near the places where they were found. Extensive collections of fossils had been made and the study of palæontology was progressing slowly. It was clearly seen that the majority of fossils belonged to species no longer living in the country where they occurred; although most geologists believed that they had become extinct, others suggested that it was possible they belonged to groups that still existed in distant parts of the world and might yet be found alive. That this suggestion was not impossible is shown by the occurrence of the lung-fish *Neoceratodus* in some of the rivers of Queensland; very closely allied species are known to occur in the Devonian and Carboniferous rocks. Within the last few weeks a fish belonging to the *Crossopterygii* is reported to have been found in the sea off the coast of South Africa; this group belongs to the faunas of the Palæozoic epochs. But when it was found that in the older rocks every species was unknown in the living state this explanation seemed insufficient.

Geologists accordingly had to deal with the problem that whole races of animals and plants had perished from the face of the earth. The fossils, for example, of the Mountain Limestone were totally different from those of the Lias, and the whole fauna and flora of the Chalk were totally different from those of the Eocene beds which immediately succeeded them. To explain these facts

recourse was had to the hypothesis of Catastrophes or Cataclysms by which at certain periods all life was exterminated.

CATASTROPHISM.

These catastrophes marked the end of geological epochs ; when a new epoch began a new fauna and flora was created. The geologists who held these views were known as Catastrophists and for a long time they dominated the science. Probably the most eminent and accomplished member of this group was the Frenchman Buffon, who was a great naturalist and held a high position in the scientific world. Buffon was an elegant writer and his books are still very readable, though their scientific value has almost vanished. In his 'Epogues de la Nature' (1778) he divides the history of the earth into seven epochs or periods starting at its first consolidation from the molten state. In the third epoch life made its appearance in the cooling oceans. The fourth epoch was characterised by volcanic outbursts and gigantic convulsions. In the fifth epoch life flourished at the poles but not at the equator. In the sixth epoch man appeared and in the seventh epoch he became the lord and master of created animals. Buffon's theories were not universally accepted, but he is probably the most eminent of the Cosmogonists, who were numerous during the last half of the eighteenth century. Cuvier, another great French naturalist and palæontologist, who succeeded Buffon, held very similar views regarding the history of creation. He did much to advance our knowledge of palæontology, and proved that in the limestones and gypsums that underlie Paris there were the fossil remains of many animals now extinct though closely related to species still living. It became clear, also, that each successive bed contained a different assemblage of fossils, some of which might be represented in a lower and older stratum, while others apparently were making their first appearance. These facts could hardly be explained by universal catastrophes and many suggestions were advanced to explain them ; as a rule they were so far-fetched and improbable that the cosmogonists became subject to ridicule and people generally regarded them as crazy. Buffon said that the geologists resembled the Roman augurs, who when they met in the streets could hardly refrain from laughing at one another.

THE DILUVIALISTS.

The favourite agencies appealed to for the extermination of faunas were volcanic eruptions, earthquakes, and deluges. Of these the deluges, probably from the example of the Noachian deluge, held the prime place. It was supposed that great floods or débâcles had swept over the face of the earth, obliterating all living creatures, changing the features of the landscape, and depositing great sheets of debris, gravel, sand, and clay. The proponents of these views were known as diluvialists. Among their eminent supporters in England was Buckland, Professor of Geology in the University of Oxford and Dean of Westminster. His 'Reliquiæ Diluvianæ' (or Remnants of the Flood) was a very popular exposition of his theories, in which he ascribed the extinction of the animals found in British caves and Pleistocene deposits to the action of the Noachian deluge. He was probably the chief British diluvialist, and before he died he began to entertain doubts of the sufficiency of his theories. The diluvialists, however, had many adherents, and it was not for fifty years after Buckland's death that they were finally routed.

Diluvianism rested upon certain well ascertained facts that were very difficult to explain. Over the Thames valley and a great part of the north of France there are vast sheets of gravel that show every evidence of having been deposited by moving water. Some of these gravels near London cap the Chalk beds at an elevation of 700 feet. In Scotland, near Edinburgh and Glasgow, there are great spreads of stony clay containing boulders of local origin and others that have been transported from the Highlands. Collectively these deposits became known as "The Drift" and we still talk of 'solid' maps and 'drift' maps. It was generally accepted that they had been distributed by floods of some kind, and even so acute an observer as Sir James Hall was inclined to share in the diluvial hypotheses. They are now known to have been deposited by moving ice-sheets and by glacial melt-waters. Strangely enough, Playfair in his 'Illustrations of the Huttonian Theory' had suggested that ice was the agency involved in the transport of erratics.

A curious corollary to the diluvial hypothesis was the theory that beneath the earth's crust there were vast chambers or caverns filled with water. This may partly have originated from the account of the Flood in Genesis which says that the fountains of the deep were opened :

possibly when the Flood subsided the waters relapsed into these caverns. Moreover these geologists had much difficulty in explaining the origin of springs. As an example we may refer to the wells in the artesian basin of Queensland and New South Wales. Some of these yield three million gallons of water per day and the water may be fairly hot and rich in mineral salts. It requires some acquaintance with geology to accept the theory that the water may be derived from rains that had fallen many years ago on distant hills. Even in recent years alternative hypotheses have found favour in some quarters. There were many other confirmatory lines of evidence. Layers of marine shells were known to occur on high mountain tops and it was inferred that at some date the waters of the sea had covered these mountains; where had they gone to if they had not sunk into the earth? The cause of the uplift of mountains was very imperfectly understood at that time. It was also assumed that on many occasions the roofs of these subterranean chambers had collapsed and that great landslips or in-thrusts had taken place in which the rocks were shattered, contorted, and set up on edge. Many disturbances in the strata were thus accounted for.

HUTTON'S 'THEORY OF THE EARTH'.

The cosmogonists, catastrophists, and diluvialists held the field towards the close of the eighteenth century, but a new day was about to dawn and their reign was nearly over. As a matter of fact the world was tired of their vagaries. The Geological Society of London was founded by a group of geologists in 1807, and one of its fundamental principles was to encourage the record of facts and observations and to discourage the promulgation of hypotheses.

In 1785 a paper appeared in the Transactions of the Royal Society of Edinburgh entitled 'Theory of the Earth', by James Hutton. Its publication occasioned no stir, possibly because the world was weary of theories of the earth, but it was really of the first importance because it is the *magna charta* of the science of geology. Hutton was a Scot, born in Edinburgh (1726), who studied medicine in Edinburgh University and subsequently in Paris and Leyden. He spent some time learning farming in Norfolk, and returned to Scotland, having inherited a property in Berwickshire, and spent the remainder of his

life in Edinburgh, where he had some interest in a chemical factory. His principal studies were geology and metaphysics, and he had a wide circle of friends, many of whom became his enthusiastic disciples; with them he made frequent excursions to scenes of geological interest in Scotland, collecting facts to illustrate the theory which was the great object of his life. He died in Edinburgh in 1797.

Hutton, being a Berwickshireman, had visited the coast section at Siccar Point, near Cockburnspath, and saw there the basal conglomerate of the Old Red Sandstone resting on the upturned edges of the folded Silurian rocks. He perceived that the pebbles of the conglomerate were derived from the underlying Silurian and that their history was the same as that of the pebbles on the beach at the base of the cliffs. On these grounds he enunciated that the Old Red was produced by the waste of the Silurian under atmospheric conditions similar to those now existing, and furthermore that all sedimentary strata were derived from the attrition of older rock masses. This was a direct contradiction to Wernerism, which held that they had been laid down from the material suspended in a primitive chaotic ocean. He went further and asserted that these processes had been going on as far back as it was possible to trace the history of the rocks of the earth's crust. The geological record, thus interpreted, shows no trace of a beginning and no sign of an end. In so doing he issued a direct challenge to the cosmogonists. Moreover, in insisting that to explain this remarkable section it was not necessary to postulate the operation of any processes not actually visible at the present day, he was the first uniformitarian, and showed that he dissented entirely from the catastrophists, who were always invoking causes that were no longer at work. To explain the geological record as shown in the sedimentary strata it was necessary to assume a practically infinite duration of time; if this were granted the phenomena might be accounted for by the action of processes such as were to be seen today on every hand. That the earth had existed for an immense period, amounting practically to eternity, was not believed by the cosmogonists, who based their opinions on the doctrines of the astronomers. It is now generally believed that the earth is at least 1,500 millions of years old, which seems ample for what we know of the changes that have taken place in its history.

If the vast accumulations of sedimentary strata were accounted for by the denudation and destruction of older rocks it was evident that the surface of the land had undergone tremendous erosion, and Hutton and his disciples did not hesitate to assert that the principal features of the landscape, such as valleys and hills, had been sculptured out by atmospheric agencies. Playfair especially insisted on this, and no point in the Huttonian doctrine was more bitterly rejected and derided than the theory of the origin of valleys. The cosmogonists and catastrophists had mostly accounted for these surface features by earthquake rifts, diluvial torrents, or the collapse of subterranean caverns. They failed to grasp the grandeur of the conception. One can appreciate their difficulties by considering the great valleys and gorges of the Blue Mountains and realising that these have been (in practically all cases) excavated during a comparatively recent geological period by the insignificant streams that flow down them. To the Wernerians such an hypothesis appeared merely preposterous.

Hutton's treatment of the problems of volcanic rocks was no less original and profound. Excellent material for study was provided to him by Arthur's Seat and Salisbury Craigs on the south side of Edinburgh. Like the vulcanists he recognised in Arthur's Seat a denuded volcanic cone of great age, with lava flows and ash beds similar to those of a recent volcano. The Wernerian doctrine that the hard basaltic rocks were subaqueous sediments he forcibly rejected. Much attention was directed to the phenomena of Salisbury Craigs, which is an intrusive sill of olivine-bearing dolerite. He and his friends recognised that this had been a molten igneous rock that had been injected into the sandstones and had probably never reached the surface. It was pointed out that the marly clays below the sill were baked to a kind of rough porcelain and that similar changes were shown by the fragments of clay included in the sill, and, what was even more significant, by the shales that lay above the sill. Consequently this was no superficial lava but a mass that congealed underground. They showed also that veins of basalt had proceeded from the sill and ramified through the superjacent rocks. A similar explanation was advanced for the dolerite dyke that forms the Cat Nick and cuts through the Salisbury Craig sill. Professor Jameson held that this dyke was a fissure that was filled by sedimentary

basaltic material from above, and Charles Darwin records that when he was a student at Edinburgh Jameson used to demonstrate the dyke to his classes and hold Hutton's theories up to ridicule. By that time, however, the Wernerian doctrines were generally discredited.

Hutton did not hesitate to carry his theoretical views still farther and to attempt to explain the origin of granite. This rock, he held, might be a molten mass which ascended through the overlying strata but solidified slowly at a great depth and by prolonged cooling became coarsely crystalline. In search of evidence he visited many granite outcrops and ultimately, in Glen Tilt, he observed a section in which the granite sent numerous veins in all directions upwards through the gneisses and limestones which form the prevailing country rocks. He was so delighted that he danced with joy and the ghillies who were with him thought he must have discovered a gold mine. The proof was complete that the granite was a plutonic igneous rock and was not older but younger than the schists. The Wernerians taught that granite was the oldest rock in every district and represented the first sediment deposited from the heated waters of the primeval ocean. From these speculations regarding the nature of granite the Huttonians came to be called Plutonists, in distinction to the Wernerians, who were called Neptunists.

On a subsequent occasion Hutton inspected the margin of the granites of Galloway and observed that towards the edge of the granite the greywackes, shales, and slates of the Silurian became converted into lustrous schists with abundant scales of newly developed mica. From this he inferred that the mica-schists and gneisses of the Highlands were probably sedimentary rocks that had been altered by heat, under great pressure, and extensively recrystallised. He had previously noticed that in Glen Tilt the rather fine-grained Highland limestones became converted into coarsely crystalline marbles where they abutted on the granite, and inferred that they had been recrystallised by the heat of the plutonic rock.

It is not without justice that Hutton is regarded as the founder of dynamical geology. He was the first to establish the science upon sound principles, and his main conclusions have successfully stood the test of time. We can appreciate the fundamental importance of his work only when we keep in mind the grotesque theories that

were current in his day, but his original memoir does not seem to have received much attention except from a small coterie of enthusiasts in Edinburgh. He was persuaded to expound his principles on a larger scale and prepared a work entitled 'Theory of the Earth' which was to be published in three volumes; of these only two were printed. The manuscript of the third remained incomplete at his death and many years later this fragment was issued in London under the editorship of Sir Archibald Geikie.

PLAYFAIR'S 'ILLUSTRATIONS OF THE HUTTONIAN THEORY'.

Among Hutton's supporters the best known was John Playfair, Professor of Natural Philosophy in the University of Edinburgh. Hutton's literary style was diffuse and unattractive, and Playfair prepared a treatise in exposition of the principles of the Huttonian theory. His book, 'Illustrations of the Huttonian Theory', was published in 1802 and is a charming account of Hutton's work written in an elegant style, perfectly lucid, and absolutely convincing. Playfair's book was well received by the scientific public but does not seem to have had a wide circulation, as it was never reprinted (except in the collected edition of Playfair's works). Playfair was an orthodox supporter of Hutton and introduced no important modifications in the Huttonian system. He specially insisted on the vast importance of denudation in modifying and shaping the features of the earth's surface. As already noted he was the first to suggest that the action of glaciers might account for many of the peculiarities of the 'drift'.

SIR JAMES HALL'S EXPERIMENTS.

One of Hutton's most intimate friends and ardent disciples was Sir James Hall of Dunglass in Berwickshire, a country gentleman of scientific tastes. He wished to support the theories of Hutton by making laboratory experiments but Hutton disapproved of this, thinking that the experiments were likely to be a failure. In deference to Hutton's opinion Hall made no experiments till Hutton died, but then he began a series that have made him famous as a geological pioneer. It had been objected that the greenstones or dolerites of Salisbury Craigs were crystalline and not glassy; all lavas, it was urged, if originally molten should be glassy and not

crystalline. Hall believed that slow cooling induced the crystalline state. By melting the dolerite in crucibles he showed that the product was glassy if rapidly cooled, but if slowly cooled it became crystalline and was indistinguishable from dolerite. His experiments on marble were even more interesting, for he took powdered chalk and by heating it in closed porcelain tubes and sealed gun barrels he produced a crystalline mass that had the structure of marble. This strongly supported Hutton's theory that granite was a plutonic rock that by its heat converted the fine grained Highland limestones into the marbles of Glen Tilt. Hall's experiments were long and difficult and showed great ingenuity and pertinacity. Other geologists had made experiments on lava before him, notably Spallanzani, but Hall deserves credit as a pioneer of experimental geology. Researches of this kind are now being carried on with the most refined physical methods in many laboratories, of which the best known is the Geophysical Laboratory of the Carnegie Institution of Washington, U.S.A.

Sir James Hall made another very simple experiment that was of the greatest importance in the theory of the earth. As a Berwickshire man he must often have seen the Silurian rocks of the cliffs near St. Abbs Head. These are folded into beautiful arches, or 'anticlines' with intervening troughs, or 'synclines'. Hall realised that these beds had once been horizontal sheets of sediment and he divined that the folding of the rocks might be due to lateral pressure. He took strips of cloth and laid them on a table; by means of boards applied to the ends of the pile he forced them into smaller compass and they took up the shape of arches and folds like the Silurian rocks of Scotland. The experiment is so simple that a child might have done it, but the importance of the underlying idea is tremendous. It shows that many of the phenomena exhibited by the older rocks of Britain might be explained by lateral pressure in the earth's crust, and thus advanced a very simple and rational explanation of two mysteries that had long perplexed geologists, (1) the folding, crushing and contortion of many rock masses especially in mountain regions, and (2) the elevation of mountain chains.

LYELL'S 'PRINCIPLES OF GEOLOGY'.

It was Charles Lyell who more than any other man gave wide publicity and authoritative exposition to the

uniformitarian doctrines of Hutton. Lyell's 'Principles of Geology' appeared in 1830 and was at once immensely popular; in ten years it had reached its sixth edition, and twelve editions had been published before the author's death in 1875. No book on geology has ever been more widely read: it was written in an easy and lucid style and no special training in natural science was needed to understand it. Lyell's mind also was extremely judicial and he never strained his arguments or overstated his evidence. His knowledge of all facts relating to geology was profound, and he had not only studied all the literature but had travelled widely and made the acquaintance of most of the active workers in geology in Europe. Each successive edition was enriched with new facts to illustrate his arguments, and even to the end of his life he was willing to reconsider his position in the light of new evidence, hence his authority was paramount. His teaching is entirely on the lines laid down by Hutton and Playfair, but he brought forward such a wealth of evidence and expounded his subject in such a masterly manner that the doctrines of Uniformitarianism swept the field and became the accepted dogmas of the science of geology.

In no small measure, however, the rapid circulation of Lyell's 'Principles' was due to the fact that the world was ready to welcome them. During the thirty years since the publication of Playfair's 'Illustrations' a great deal of active geological research had been carried on. The Geological Society of London had been founded in 1807 and its published Transactions contained many papers of high merit. In them there was little trace of the theories of the cosmogonists and catastrophists but a vast body of facts carefully observed, and recorded. Among the prominent members of the Society were Buckland, Conybeare, Sedgwick, Murchison, De la Beche, Godwin Austen, Daubeny, MacCulloch, Lonsdale, Phillips, Lyell and Fitton, all of whom were geologists of the first rank. The discussion that took place over the papers read to the Society were of absorbing interest, and there was no doubt that Lyell, who was in turn Secretary and President of the Society, received much of his geological training in this way. When, in 1830, Charles Darwin started on his voyage in the "Beagle", he took with him the newly published first volume of Lyell's 'Principles'. Darwin had studied geology under Jameson in Edinburgh, but had only acquired a disgust for Wernerianism as expounded by its

principal British upholder. Lyell's book, however, inspired Darwin with a new interest in the subject and set him thinking on geological problems. To this, no doubt, we owe his profound theory of the origin of coral reefs, which after a hundred years of criticism still maintains its position, and has been strongly supported by the researches of Edgeworth David at Funafuti, and the scientific workers on the Australian Barrier Reef. It seems also reasonable that the theory of Evolution through Natural Selection may be considered an extension of the principles of uniformitarianism to the organic world, and a rejection of the theories of catastrophism and special creation against which Lyell contended. Lyell, though at first sceptical, accepted Darwin's views and became one of the most influential supporters of evolution.

WILLIAM SMITH AND STRATIGRAPHICAL GEOLOGY.

While the principles of dynamical geology and the processes by which rocks are formed and destroyed were thus being established during the early years of the nineteenth century, great progress had also been made in stratigraphy and palæontology. The Wernerians and Huttonians had not been much interested in fossils, but in England the study of the fossiliferous rocks had yielded results of the highest possible importance. This advance is linked with the name of William Smith, one of the greatest untutored geniuses that Britain has produced, a man who with little training and entirely by the force of his powers of observation and reasoning established the principles of stratigraphical geology on a basis that has proved everlasting.

Smith, the son of an Oxfordshire farmer, received his early education at a village school, and was apprenticed to a land surveyor. He ultimately became a civil engineer and spent his active life in surveying and constructing canals, bridges, roads, drains, and tunnels. This work brought him constantly into connection with rocks, quarries, and cuttings, and his natural powers of observation had full play. He eagerly collected fossils, noting at the same time the rocks in which they occurred and the locality where they were obtained. The neighbourhood of Bath, where he lived, is very rich in geological formations, and the Carboniferous, the Jurassic, and the Cretaceous, all very fossiliferous, were accessible to his inspection. In 1791 when he was 22 years of age he had recognised the

position of the Lias, the Trias, and the Carboniferous in his district. Urged on by an uncontrollable impulse he neglected no opportunity to extend his observations, and, as his daily work involved much travelling, he became acquainted with a large part of the west of England. His friends regarded his foible as harmless and uninteresting, but he was convinced of the value of his results and persevered in his task, though there was no one with whom he could share his enthusiasm. In 1799 he met some clergymen who took an intelligent interest in geology, and he astonished them by producing a table of the strata from the Carboniferous to the Cretaceous, giving the subdivision of the formations, their thickness, lithology, and characteristic fossils. Copies of this table were made and circulated among geologists. Nothing so complete and convincing had been seen before. It marks the beginning of scientific stratigraphical geology and entitles Smith to the title of Father of British Stratigraphy. That a man who possessed only an elementary education, had of his own initiative, and entirely unassisted, accomplished an achievement so difficult, so original, and so important, is one of the wonders of the history of science.

Other geologists in Germany, France, and England had noted that certain formations or even sub-formations contained assemblages of fossils peculiar to themselves and apparently not found elsewhere. Cuvier, Buffon, Soulavie, Brongniart and others had devoted much time to the study of the fossil faunas of particular deposits. Smith was not a palæontologist and was not especially interested in the structure and zoological affinities of the fossils that he collected. Their stratigraphical significance was his principal concern; he had grasped the important fact that each formation had its distinctive fossil remains and that even though the lithology differed in different localities, the strata could be identified by their fossils. The various members of the Jurassic and Cretaceous could be traced across England from the south coast to the north-east coast and recognised with certainty by their characteristic fossils. The easterly dip of the strata entailed an upward succession of outcrops from west to east, and each peculiar belt of rock yielded a type of country that was familiar to a practised eye. For the various formations which he was the first to separate and identify, Smith used local names such as Gault, Cornbrash,

Coral Rag, Portland Rock, Oxford Clay, and that most of them are still in use testifies to the accuracy of his discriminations. As a surveyor Smith was familiar with maps and sections, and in 1801 he planned a geological map of England. This work was finished in 1812 and published in 1815 in 21 sheets on the scale of one inch to five miles. The map was hand-coloured under Smith's supervision, and successive copies show differences that prove that he was continually enlarging and correcting his knowledge of English stratigraphy. The amount of information contained in this map is enormous and the work is one of the classics of English science. With very little help Smith had accomplished an achievement that was entirely unparalleled. It is astonishing how little alteration is necessary in Smith's map, even at the present day. Founded on correct principles and executed with the greatest diligence and accuracy, it placed the stratigraphy and much of the topography of the geology of England before the scientific world. It has served as a model for all subsequent geological maps.

William Smith also projected a book to explain the principles on which his map was founded but the publication of this was never completed. He also drew a geological section across England from London to Snowdon in Wales, and wrote a short pamphlet explanatory of his great map. He died in Yorkshire in 1839. His work was done, and so well done that it carried conviction to all who were competent to understand its meaning and has never suffered criticism of a damaging nature. This map gave a great stimulus to geological cartography as it was clear that the true methods had been established, and Greenough and the Geological Society of London published a geological map of England in 1822, using most of Smith's results, with improvements in the topography and engraving. MacCulloch also was engaged on the preparation of a geological map of Scotland (partly under government auspices) but this did not appear till 1840. Richard Griffith prepared a useful geological map of Ireland which came from the press in 1834 and 1838. The knowledge of the regional geology of England was making very rapid progress and a useful summary was issued by Conybeare and Phillips in 1822, adopting the results of W. Smith's work almost without modification, and giving a general conspectus of historical geology.

THE WORK OF W. B. CLARKE.

It is interesting to note that Smith's methods of determining the age of geological strata were employed with great success in Australia by W. B. Clarke. As the pioneer of Australian stratigraphical geology he fully recognised the value of fossil evidence. He entered into a controversy with Sir Frederick McCoy, no mean opponent, regarding the age of the coal-bearing strata of New South Wales. McCoy had stated that they were Mesozoic, but Clarke by collecting fossils extensively was able to establish that they belonged to older and deeper horizons. Clarke did not confine his attention to the coal-bearing strata. He made many collections of fossils, wherever they could be found, and sent them in large numbers to British, French, and Belgian palæontologists for accurate determination. In this way he succeeded in proving that in New South Wales there were strata of Ordovician, Silurian, Devonian, Carboniferous, and Permian age. He trusted entirely to the evidence of the fossils, and he was not deceived: subsequent work has confirmed the truth of his conclusions, and he followed faithfully in the footsteps of William Smith. The Australian fossils, of course, are not always the same as those found in England, but the general aspect of the successive faunas is distinctive and characteristic.

MURCHISON AND SEDGWICK.

By 1830 then, when the first volume of Lyell's 'Principles' made its appearance from the press, the main foundations of dynamical geology, stratigraphical geology, and the regional geology of England had been well and truly laid. Though an immense amount of detailed work had yet to be done, most of the rocks from the Carboniferous upwards had been put into their correct sequence, and their distribution was approximately known. It was known, however, that below the Carboniferous there were still older rocks whose history had not been solved. The Old Red Sandstone, for example, occupied large areas on the Welsh borderland and in Scotland: in Devonshire at Torquay and elsewhere there were fossiliferous limestones of great age, and in north Wales, Cumberland and Galloway there were slates and grits much broken and contorted and belonging to none of the recognised geological periods. In some of these rocks fossils had been found, but they were comparatively rare and often in bad preservation.

British geologists set themselves the task of reading the riddle of these formations, and their success marked a new epoch in the geology of the older rocks.

Murchison was a Highlander, the owner of a hereditary estate in Ross-shire. He served as an officer under Wellington in the Peninsula, but resigned when the war was over, and for a time was an enthusiastic sportsman and rider to hounds. Of this he tired, however, and, on the persuasion of his wife, took up the study of geology. A man of boundless energy and great determination, he made rapid progress: for a short time he studied under Buckland at Oxford, and soon he made an alliance with Sedgwick that was to be productive of most notable results.

Sedgwick, the son of a Cumberland vicar, was educated at Trinity College, Cambridge, and somewhat to his own astonishment, for he knew little geology, was elected Professor of Geology in Cambridge in the year 1818. At that time he was thirty-three years of age, and he at once took up geological research with great vigour and enthusiasm. He was a brilliant lecturer and a most inspiring teacher, and, with Murchison, he wrote some papers on English secondary rocks. He also investigated the geology of Cornwall, but his earliest efforts had something of a Wernerian flavour. In 1827 he and Murchison visited the north of Scotland and examined the Old Red Sandstone. It was not till 1831, however, that Sedgwick and Murchison extended their explorations to Wales, and tackled the problem of the ancient rocks generally known at that time as the 'greywacke' formation. Starting from the base of the Old Red Sandstone in Shropshire and Herefordshire, Murchison rapidly identified a number of stratigraphical groups to which he gave local names such as Wenlock and Ludlow, and ascertained that they had characteristic fossil faunas. Year by year he pushed his investigations farther west into lower stratigraphical series, to each of which he gave local names, and found that each possessed a distinctive assemblage of fossils. In 1835 he adopted the name Silurian System for the whole series of rocks in north and eastern Wales which he had been investigating and describing, and in 1839 he published a complete account of them in his book 'The Silurian System'. The description of the fossils was done principally by Lonsdale and Sowerby.

Sedgwick meanwhile had been at work in north Wales, in the country around Snowdon and to the west. He too

had discovered a stratigraphical succession, though the rocks were poor in fossils, and to these strata he gave the name Cambrian System. His series had no definite base or summit, but it was generally assumed that the Cambrian underlay Murchison's Silurian. No definite division line was laid down between them. In course of time it was proved that these systems overlapped, and the top of Sedgwick's Cambrian was the bottom of Murchison's Silurian. A bitter controversy ensued in which Murchison for a time seemed to have the upper hand, but ultimately it was recognised that the Cambrian and Silurian Systems were each entitled to recognition, and they are now universally accepted. It is a great tribute to the energy and ability of these two pioneers that almost single-handed they cleared up one of the most difficult problems of stratigraphical geology, and established and named two of the principal geological systems.

The controversy between Murchison and Sedgwick regarding the place of the Lower Silurian rocks was both regrettable and undignified. It was solved ultimately, with universal approval, by Charles Lapworth. This distinguished geologist, though born in England, did his first important researches in Scotland. His memoirs on the Silurian rocks of Scotland and their fossils are classics of the first order, showing extraordinary penetration that amounted to genius. Subsequently he was Professor of Geology in Birmingham University, and made great contributions to the geology of the older rocks of the west of England, and the problems of Highland tectonics. Lapworth proposed that Murchison's Lower Silurian should be called Ordovician, after the name of an old Welsh clan, and this suggestion was so reasonable and satisfactory that the term passed into general use.

In Devon and Cornwall there is a terrain of ancient rocks that presented many problems difficult of solution. Intense folding and partial recrystallisation together with metamorphism of the contact type around extensive intrusions of granite had obliterated their original fossil contents and confused their stratigraphical relations. It was known that in this territory there were rocks of Carboniferous age, containing plants and fossils typical of that formation, and Charles Peach had found on the south coast some fossiliferous beds that seemed to be Silurian (or Ordovician). But the dominant rocks of this province had yielded no fossils, and were classed by De la Beche,

who was engaged in mapping them, under the collective term 'greywacke'. It was thought that some of them might be Cambrian, or older. Sedgwick and Murchison made a gallant attempt to solve the mystery, and came to the conclusion that in this area there might be strata intermediate in age between the Silurian and the Carboniferous. It was a bold suggestion, because the Cornish rocks had no close resemblance to the Old Red Sandstone of Wales, which presumably occupied the same stratigraphical position. But Lonsdale, a skilful palæontologist, undertook the inspection of the fossils that occur in the limestone of Torquay, and announced that they were neither Carboniferous nor Silurian, but belonged to an intermediate period. In this way the Devonian System came to be established, and subsequently rocks of this age were proved to occur in several parts of Germany and in Bohemia, where they yielded large suites of well preserved fossils.

In 1841, after his return from Russia, where he had made a geological expedition on the invitation of the Czar, Murchison announced that in the province of Perm there were wide areas of rocks corresponding closely with those known in England as the Magnesian Limestone and in Germany as the Dyas. He proposed to call this formation the Permian, and this name rapidly passed into general use.

We see accordingly that of the Palæozoic System, the Cambrian (Sedgwick), the Ordovician (Lapworth), the Silurian (Murchison), the Devonian (Sedgwick and Murchison), and the Permian (Murchison), all have names applied to them by British geologists, who either discovered them or were the first to assign them to their correct place in the geological sequence. We may add that the terms Palæozoic, Mesozoic, and Cainozoic were first suggested by Phillips, while Lyell (with Deshayes) was the first to classify the Cainozoic into Eocene, Miocene, Pliocene, and Pleistocene. These facts indicate how large a part the British geologists of this period played in determining the nomenclature of stratigraphical geology. In fact British geologists were in advance of their European colleagues in this field, and we shall not be wrong in supposing that the reason was that they had more fully and readily appreciated the fundamental importance of the teachings of William Smith, on which all progress in stratigraphy was founded.

By the year 1840 the science of stratigraphical geology was firmly established, and a vast number of able workers was carrying on research in all parts of Europe and America. In Australia the beginnings of geological investigation had been made, and in 1875 Strzelecki and W. B. Clarke were at work in New South Wales. Once the correct methods had been found, and the fundamental classifications determined, progress was rapid and sure. The importance of geology began to be recognised by governments. The first official Geological Survey was that of Great Britain, which Sir Henry de la Beche persuaded the British Government to create in 1835. Since that time every important state and dominion have followed the example, and today there are over a hundred official geological surveys.

GLACIAL GEOLOGY.

Much uncertainty still prevailed regarding the origin of the 'diluvial' deposits that covered so large an area of Britain and were obviously laid down during one of the latest stages of our geological history. At last light was thrown upon the problem by the investigations of alpine geologists. Among these Venetz, Charpentier and Agassiz were the leaders; they proved convincingly that at a not very distant date the glaciers of the Alps had had a much wider extension, and had spread over the plains below the mountains, leaving great heaps of debris with striated transported boulders; in fact that there had been an Ice Age during the Pleistocene period. In 1840 Agassiz attended the meeting of the British Association at Glasgow, and was taken to see a remarkable striated rock surface at Blackford Hill near Edinburgh. On inspecting it he exclaimed immediately "Certainly this is the work of ice". Scottish geologists very promptly followed up the suggestion. They found abundant evidence of its truth, as ice-scratched boulders and rock surfaces were everywhere present, and in the mountain valleys there were moraines, perched blocks, and numerous erratics. Among the most enthusiastic workers in this field were Sir Andrew Ramsay and Sir Archibald Geikie. Ramsay described the ancient glaciers of the valleys of north Wales; Geikie studied the glacial drift of Scotland. The new theories rapidly made progress, but for a time there were many who believed that the glacial drift of England had been deposited by floating ice and not by ice-sheets. Ramsay made the

suggestion that there had been Ice Ages in previous geological epochs such as the Permian. His views were not generally approved as the evidence was considered insufficient, but it is now known that there was a Permian Ice Age in Australia, India, South Africa, and South America. Still earlier Ice Ages have been discovered, and the work of Howchin and Sir Douglas Mawson has proved that in Cambrian (or Pre-Cambrian) times there was extensive glaciation in South Australia.

James Croll and James Geikie were so bold as to maintain that the Quaternary or Pleistocene Ice Age was not simple but complex, and that there were several interglacial periods of mild climate. Evidence in support of this theory was obtained in North America, Switzerland, Germany, and Denmark, but English geologists were sceptical. It is now generally acknowledged, however, that it is correct.

CONCLUSION.

It is universally acknowledged that British scientists in the early years of the nineteenth century took a leading part in founding the science of geology. Hutton was the pioneer of dynamical geology, William Smith of stratigraphy, and Sir James Hall of experimental geology, and when the correct methods and fundamental principles had been discovered there was rapid progress, and Sedgwick and Murchison with many others, such as Logan, Lyell, Lonsdale, Salter, Fitton, De la Beche, and Phillips in a very short time produced results of the highest value. By 1835, when Lyell's 'Principles' was completed, the science had an entirely modern aspect, and many of the main problems had been solved. In these years British geologists led the world, as in Germany, Wernerianism, and, in France, Catastrophism were not yet extinct, but were dying a slow death. With their gradual disappearance the triumph of Uniformitarianism was finally achieved, and, though it is recognised that there are limitations to its application, the general principle holds good that the explanation of the past history of the earth must first be sought in the processes that we see going on around us at the present day.

REFRACTIVE INDEX DETERMINATIONS IN THE
INFRA-RED FOR PARALLEL-SIDED
SPECIMENS OF GLASS.

By N. R. HANSEN, B.Sc.

Communicated by PROFESSOR O. U. VONWILLER.

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During investigations into the transmission of obliquely incident infra-red radiation through a glass plate, it was found desirable to have a fairly accurate knowledge of the refractive index of the glass for a given wave-length, the only specimen available being the parallel-sided plate of thickness approximately 2 mm. A method is described in this paper which gives satisfactory results.

The plate used was a sample of one of Schott's glasses, 5 cm. square, described as BG 18, with melt number S 1154. Measurement showed it to be slightly wedge-shaped, the mean thickness being 2.09 mm., with extreme values 2.076 and 2.100 mm.

Apparatus was arranged as shown in Fig. 1. The source of radiation was a Nernst lamp N run at 200 watts. The focal length of a quartz lens L was found by optical means for red light and then, from this and a knowledge of the dispersion of quartz, for a wave-length of 2.2μ . L was then placed at this latter distance from N, so as to collimate the light of this particular region of the infra-red. Thus a fairly uniform beam of parallel light fell upon the diaphragm D, in which was a slit S_1 . This slit was attached to a carrier which was movable by a micrometer screw in a direction perpendicular to the length of the slit and to the direction of the incident light. Beyond S_1 was the slit S_2 of a Hilger infra-red spectrometer (furnished with Moll thermal relay amplifier) which, for preliminary investigations, was set at a wave-length of 2.22μ , where the glass specimen was most transparent. Between S_1 and S_2 was a rotating graduated stand for holding the glass plate P, so that the latter could be inserted in the path of the rays at any desired obliquity.

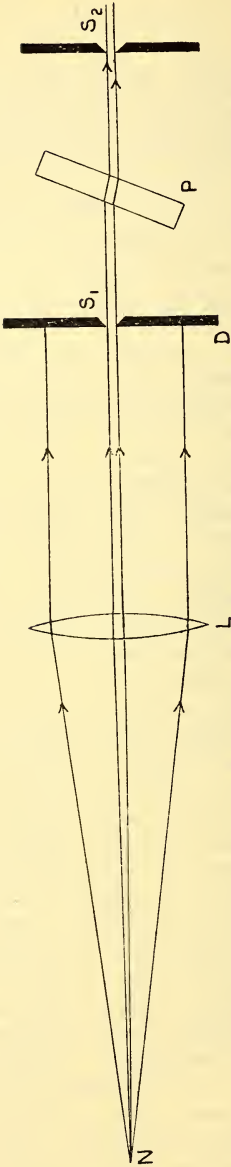


Fig. 1.

In the absence of P, and in the general case with S_1 , S_2 and N non-collinear, the galvanometer connected to the spectrometer thermopile indicated zero intensity; but as S_1 was moved with the micrometer so as to come nearly in line with S_2 and N, the galvanometer was deflected, the deflections increasing to a maximum and then falling off again with the movement of S_1 . Observations were made of the galvanometer readings every 0.05 mm., as the micrometer was turned. The readings were plotted against the micrometer position, a perfectly symmetrical curve being obtained. Such curves are shown in Fig. 2.

On insertion of the obliquely placed glass between the two slits the emergent beam suffers a small lateral displacement δ from the original position, where

$$\delta = \frac{a \sin i (\sqrt{n^2 - \sin^2 i} - \cos i)}{\sqrt{n^2 - \sin^2 i}}$$

“ a ” being the thickness of the glass plate.

Hence when S_1 was moved by means of the micrometer, and galvanometer deflections observed for 0.05 mm. movements of S_1 , a curve similar to the abovementioned was obtained, but displaced slightly to one side and also diminished in height owing to absorption in the glass. By rotating the glass plate so as to give an equal angle of incidence in the opposite sense, a third curve was obtained displaced by an equivalent distance on the opposite side of the first.

Actual curves obtained are shown in Fig. 2. Curve I indicates galvanometer deflections for successive micrometer positions in the absence of the glass. Curves II and III are those displaced to either side of I when the light is incident at an angle of 30° . IV and V are the corresponding curves for 60° incidence.

The “ δ ” of the above formula is the difference between the abscissæ corresponding to the maxima of curves I and II, I and IV, and so on. It was, however, impossible to fix the maxima to the desirable degree of accuracy, for the observed galvanometer readings were doubtful to the extent of about 1%. An error of this magnitude is, however, less serious along the sloping sides of the curves. Thus on choosing points A, B or A', B' at equal heights and bisecting the intervals to give points X, X', it was found that the abscissæ of the points X, X', . . . were independent of their ordinates, so that the maxima of the various curves could be found by determining points such as X.

This symmetry was found to be well maintained for all angles of incidence investigated (0° – 75°); and even when wave-lengths well removed from the 2.2μ for which the apparatus was arranged were used, there was no appreciable departure from symmetry, so that a perfectly collimated beam is apparently not essential.

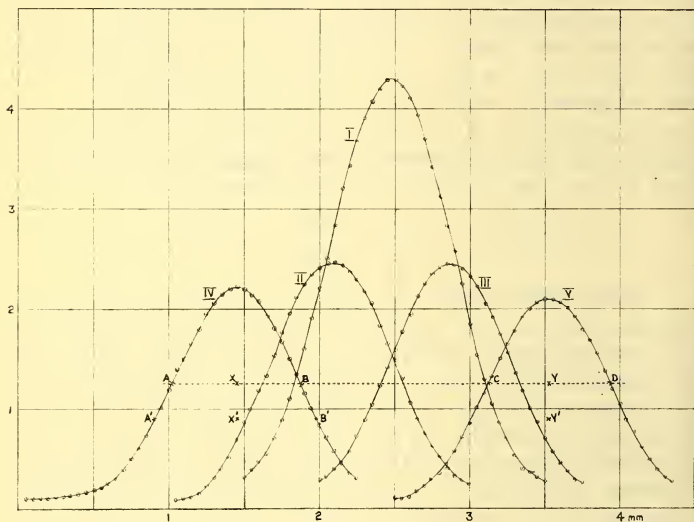


Fig. 2.—Variation of Galvanometer Deflections with movement of Slit.

Ordinates are galvanometer deflections in cm.

Abscissæ are micrometer readings in mm. with an arbitrary zero.

$$\lambda = 2.2\mu.$$

Details.—Curve I: No glass.

Curves II and III: Angle of incidence = 30° .

Curves IV and V: Angle of incidence = 60° .

To minimise errors resulting from the determination of the points X, the quantity " δ " was taken to be half of XY. From a knowledge of the angle of incidence, the refractive index " n " was calculated from the formula for angles of incidence 30° , 45° and 60° . (The second set is omitted from Fig. 2 to avoid complicating it.) The three values of " n " so obtained agreed to within the estimated experimental error. Subsequent investigations were therefore restricted to 45° incidence. Under these conditions values of δ were obtained as before for wave-lengths between

1.4μ and 2.8μ . Beyond these limits the low emission of the Nernst lamp and the increasing opacity of the glass (see Fig. 3) made the curves too flat to allow of " δ " being found with sufficient accuracy to be of value.

Even within the range indicated the method left much to be desired. Firstly, the very fact of the two curves having to be drawn before δ can be found makes the process involve at least a half-hour. (The difference in heights of curves IV and V is accounted for by changes in the Nernst lamp current during the interval between taking the two sets of readings.) Secondly, the thermopile-relay-galvanometer system is very sensitive to external influences, and it is difficult to allow for fluctuations in the position of the undeflected galvanometer during the time necessary to take the readings required for a curve.

Results were greatly expedited and improved by a modification depending on the constancy of the abscissae of X, X'. Some deflection of the galvanometer, about half the maximum, was decided upon in advance, and micrometer readings were taken for those positions of the slit S_1 which gave rise to the chosen deflections. Thus four points such as A, B, C, D were determined within a few minutes. Bisecting the intervals AB, CD gave points X, Y and so δ as before. Thus the necessity for curve-drawing was eliminated, but it must be emphasised that, before this quicker method is adopted, complete curves should be drawn and their symmetry verified.

The earlier method usually involved a probable error of about 0.005 mm. in fixing the position of the maximum of any one curve, so the error in δ , which is half the distance between two maxima, is of the same order. Thus, since δ was usually of the order of 0.65 mm. for 45° incidence, its order of accuracy was about 1 in 150. This means that the calculated " n " has an order of accuracy of 1 in 200. The newer method, as indicated by the variation in the value of δ obtained by successive attempts at the same wave-length and obliquity, gave an order of accuracy, except at extreme wave-lengths, of 1 in 500 for the mean of measurements at any one wave-length. An inspection of line A in Fig. 3 shows that " n " can probably be given to an accuracy of 1 in 1,000.

This latter method was applied to a determination of the refractive index for wave-lengths between 1.4μ and 2.8μ . The results are summarised in the dispersion curve of Fig. 3. For comparison is shown the transmission curve

of the glass, uncorrected for reflections. The determinations were limited at these wave-lengths by the light intensity becoming too low, but the limits may be extended somewhat by attention to the geometry of the arrangement.

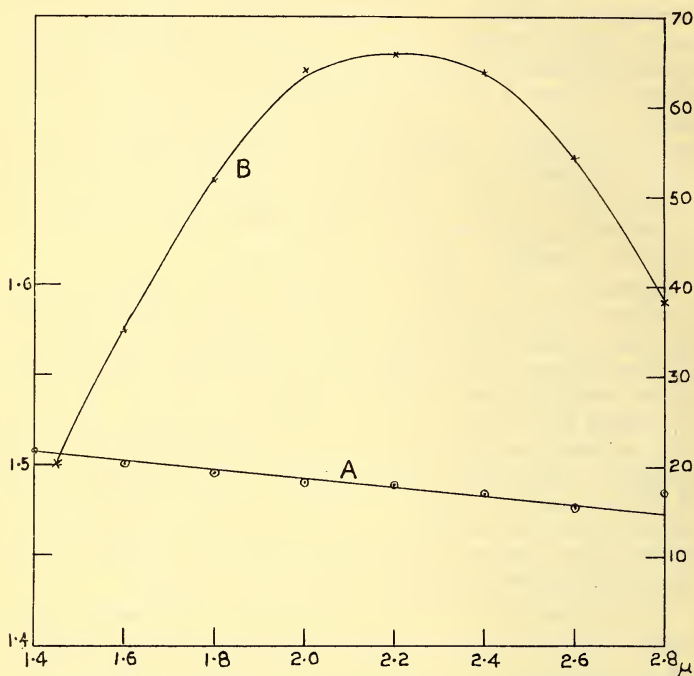


Fig. 3.—Variation of Refractive Index and of Transparency with Wave-length.

A. Dispersion curve—indices of refraction on left.

B. Transparency curve—percentage transmission for normal incidence on right.

The slits S_1 , S_2 had widths 0.29 mm. and 0.43 mm. respectively (although truncation of the curves should be a minimum when the two slits are of equal width). Hence only a very small fraction of the collimated light finally passes through S_2 to affect the thermopile. Interposition of a short focus lens or mirror at a suitable place in the system should allow of considerable concentration of the beam incident on D. This should not be pursued too far,

however, for if the beam is too narrow the intensity of light passing through S_1 would change as the micrometer is advanced and the symmetry of the curves, upon which the whole method depends, would be destroyed.

This work was carried out in the Physical Laboratory of the University of Sydney. The Hilger infra-red spectrometer and also the thermal relay, without which the measurements could not have been made, were the gift of the late G. H. Bosch, Esq. Appreciation must also be expressed for the help of Professor O. U. Vonwiller, who directed the investigation throughout.

SUMMARY.

A method is described for the determination of the refractive index of parallel-sided plates of glass, for infra-red wave-lengths, by measuring the distance through which a narrow parallel beam of radiation is displaced laterally when passing through the glass at oblique incidence.

With a plate of Schott's BG 18 glass 2 mm. thick, the refractive index was determined over the range 1.4μ - 2.8μ , with an accuracy of at least one in 500.

THE REACTION OF 3,5-DINITROBENZOIC ACID WITH ALKALI.

II. THE MAIN PRODUCT OF THE REACTION, 3,3'-DINITRO- 5,5'-DICARBOXY-AZOXYBENZENE.

By ADOLPH BOLLIGER, Ph.D., A.A.C.I.,
and FRITZ REUTER, Ph.D., A.A.C.I.

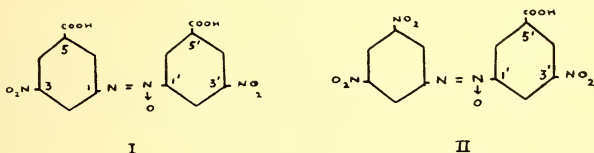
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In a previous communication (Bolliger and Reuter, *THIS JOURNAL*, 1939, 72, 329) it was shown that the compound responsible for the red colour formed by the action of strong alkali on 3,5-dinitrobenzoic acid is identical with 2,3-dihydroxy-5-nitro-benzoic acid. It is produced only in a comparatively small yield, and Shukoff (*Ber. dtsh. chem. Ges.*, 1895, 28, 1802) was mistaken in assigning to it the structure of an azoxy-pyrogallic acid. The main product of this reaction (I) had also been isolated and studied by Shukoff (*l.c.*). He described I as a practically white amorphous substance, melting above 200° C. with decomposition, which is practically insoluble in cold and hot water, benzene and ether, but very readily soluble in alcohol. It dissolves in sodium hydroxide to form a lightly brown-coloured solution and excess alkali precipitates its sodium salt in the form of voluminous jelly-like flakes. Shukoff determined the molecular formula of I as $C_{14}H_8O_9N_4$ and proposed for it the structure of a 3,3'-dinitro-5,5'-dicarboxy-azoxybenzene. He was, however, unable to advance any further evidence in support of this structure.

In connection with our previous research (*l.c.*) we obtained considerable quantities of I which we further examined.

Under the experimental conditions used for obtaining an optimal yield of the dihydroxy-nitrobenzoic acid as described in our first communication, considerable quantities of I are formed, which, however, are contaminated with coloured impurities from which I is difficult to isolate in a pure state. It is, however, possible to obtain a practically colourless sodium salt of I from a reaction mixture as well

as a fair yield of 2,3-dihydroxy-5-nitrobenzoic acid, if a comparatively lower concentration of alkali is used and allowed to act for a shorter time on the dinitro-benzoic acid. Optimal conditions for the preparation of I are given in the experimental part. I, isolated from the crude sodium salt, can be purified by recrystallisation from a large volume of boiling anisole, from which it separates on cooling in faintly cream-coloured crystalline aggregates, melting at 288° with decomposition. It may also be purified by the careful addition of water to a solution in alcohol or dioxan. It analyses for $C_{14}H_8O_9N_4$, confirming Shukoff's result. In alcoholic solution it can be titrated with aqueous alkali, using phenolphthalein as indicator, and an equivalent weight is obtained, indicating the presence of two carboxylic acid radicles in the molecule. I is soluble in aqueous alkali, giving a practically colourless solution, and excess alkali precipitates a colourless di-sodium salt in jelly-like flakes. I forms esters and the methyl and ethyl esters have been prepared, melting at 137° and 116° respectively.



Numerous attempts were made to reduce I but under no conditions were products obtained which could be further purified or identified. Yellow, high-melting, amorphous or microcrystalline products were formed which were practically insoluble in all solvents tried, when I was reduced with stannous chloride in concentrated hydrochloric acid solution or in a solution of stannous chloride in glacial acetic acid saturated with hydrochloric acid gas. Reduction was also tried with titanium trichloride, sodium hydrosulphite, and ammonium sulphide with no better success. In a few of these experiments, however, the formation of small quantities of a meta-diamine could be shown by a positive Griess-reaction, i.e. the formation of an intense yellow-brown coloration on the addition of acid and sodium nitrite to the reduction products or reducing solution after removal of excess reducing agent. These results can be taken to support the structure of a 3,3'-dinitro-5,5'-dicarboxy-azoxybenzene for I on account

of their analogy to the unavailing attempts of other authors to reduce azoxy-benzoic acids to the corresponding amines.

Also by reason of analogy the formation of an azoxy compound can be expected by the action of alkali on a nitro-compound. (Lobry de Bruyn, *Rec.*, 1894, 13, 101.) However, in contrast to other nitro compounds, the ease with which 3,5-dinitro benzoic acid is converted into I is worthy of mention. This is indicated by the speed of the reaction and the yield, which amounts to about 50% of the 3,5'-dinitro benzoic acid used under comparatively mild conditions. Even from a 2N sodium hydroxide solution containing a suspension of sodium dinitro benzoate I can be obtained if the mixture is kept at room temperature for several days. The yield, however, is only about 20% after the suspension has been standing for one week.

The Wallach transformation of I to a hydroxy-azo compound by the action of hot concentrated sulphuric acid could be effected only in traces, if at all. This may be explained by the configuration of I offering considerable resistance to the rearrangement on account of steric hindrance.

The action of concentrated nitric acid on I is interesting. I can be recrystallised from ordinary concentrated nitric acid ($d = 1.4$). However, if the boiling with the acid is prolonged, traces of a new compound are formed as indicated by the colouration of a solution of the recrystallised I in sodium hydroxide. If I is boiled for about sixteen hours in stronger nitric acid ($d = 1.48$) a good yield is obtained of a new compound which analyses for $C_{13}H_7O_9N_6$ (II). This molecular formula indicates that one nitro group has entered the molecule of I and one carboxyl group has been eliminated.

The presence of a carboxylic acid radicle in the molecule is shown by the formation of an ammonium salt $C_{13}H_{10}O_9N_6$ and the fact that carbon dioxide was given off during the reaction gives evidence of the elimination of a carboxylic radicle from I in the formation of II. On account of the meta directing power of the nitro-radicle we feel justified in assigning the constitution of 3'-carboxy-3,5,5'-trinitro-azoxybenzene to II. In all probability the change has taken place in the benzene nucleus attached to that nitrogen of the azoxy-group which carries no oxygen. This follows from the observations of Angeli (On the Constitution of Azoxy Compounds, Stuttgart, 1913),

who has shown that this benzene nucleus is preferably involved in any reaction carried out with azoxy compounds.

Of further and probably practical significance is the behaviour of I, its methyl and ethyl esters, and II towards acetone and other methyl ketones in the Janowski reaction,¹ because they give a colour reaction similar to that of meta dinitro benzene and 3,5-dinitro benzoic acid. In addition a number of other azoxy derivatives have been tested with regard to their ability to give a colour with methyl ketones in alkaline solution. Only 3,3'-dinitro azoxy-benzene and 2-nitro azoxy benzene also gave positive results, while azoxy benzene, azoxy anisole, 4'-carboxy azoxy benzene and 3,3'-dicarboxy azoxy benzene gave negative results. This indicates that in azoxy compounds at least one nitro-group is conditional for this colour reaction to take place. Further details of these reactions, such as sensitivity, will be given in another communication. It is, however, noteworthy that I gives colourless solutions with alkali of any concentration, whereas the other nitro compounds suitable for this reaction, the detection of methyl ketones, themselves give coloured solutions on the addition of caustic alkali.

With regard to the question whether I is formed first when dinitro benzoic acid reacts in the presence of methyl ketones and caustic alkali, and whether this compound must be assumed as an intermediate, we have come to the conclusion that this is not the case. The addition of 0.1 N sodium hydroxide is sufficient to obtain in less than a minute a colour reaction with dinitro benzoic acid and certain methyl ketones, such as acetone, creatinine, etc. At such a small alkali concentration and in such a short time dinitro benzoic acid is not altered. Neither can 2,3-dihydroxy 5-nitro benzoic acid, which is also obtained by the action of strong alkali on 3,5-dinitro benzoic acid (*l.c.*), be considered as an intermediate, for the reason already mentioned as well as for the fact that it does not react with methyl ketones.

EXPERIMENTAL.

The preparation of I. 3,5-dinitrobenzoic acid (20 g.) is dissolved in a mixture of N/2 aqueous sodium hydroxide (200 ml.) and water (100 ml.). The filtered solution is

¹ Houben-Weyl: Die Methoden der organischen Chemie, Volume IV, p. 192, Leipzig, 1924.

slowly poured with stirring into 500 ml. of approximately 10-11 N sodium hydroxide. A voluminous precipitate is formed in the course of a few minutes and the reaction mixture takes on an intense red colour. It is allowed to stand for 3-4 hours at room temperature and then is filtered on a large Büchner funnel through a Whatman filter paper No. 54. This paper was found to be well suited for this purpose if care is taken in using a sufficiently large filter paper to allow for the shrinkage that takes place by the action of the strongly alkaline solution. For instance a 12 cm. filter paper had to be used for a Büchner funnel of 11 cm. internal diameter. The filtration under these conditions takes about 8 hours using a water jet pump. The filter cake is dissolved in water (approx. 300 ml.) and I precipitated by the addition of 2 N hydrochloric acid. Yield after drying *in vacuo* 8.4 g., corresponding to a 48% yield. After recrystallisation from anisole and alcohol the substance consists of faintly cream-coloured small needles. M.P. 288° C.

Found: C, 44.84; H, 2.25; N, 14.97%. $C_{14}H_8O_9N_4$ requires C, 44.63; H, 2.14; N, 14.90%.

Equivalent weight found: 186, 190; required, 188.

The red mother liquor after appropriate treatment (Bolliger and Reuter, *l.c.*) yields about 1.8 gm. of potassium 2,3-dihydroxy-5-nitro-benzoate.

Methyl Ester of I (Dimethyl 3,3'-dinitro-azoxybenzene-5,5'-dicarboxylate). A solution of 5 g. of I in about 150 c.c. of methyl alcohol was saturated with anhydrous hydrochloric acid gas. A brownish precipitate separated from the hot solution which, on cooling increased and which consisted mostly of a mixture of the methyl ester of I and a tarry substance. A further amount of the ester was obtained by pouring the filtrate from the precipitate into water. The combined precipitates were recrystallised from methyl alcohol, care being taken to separate the crystalline ester from the tarry substance which is sparingly soluble in methyl alcohol. After repeated recrystallisation from methyl alcohol the ester consisted of fine cream coloured needles. M.P. 137° C.

Found: N, 13.90%. $C_{16}H_{12}O_9N_4$ requires 13.86%.

Ethyl Ester of I (Diethyl 3,3'-dinitro azoxybenzene-5,5'-dicarboxylate). The ethyl ester of I was prepared in an analogous manner. Faintly yellow needles were

obtained after repeated recrystallisation from ethyl alcohol. M.P. 116°C .

Found : N, 13.35%. $\text{C}_{18}\text{H}_{16}\text{O}_9$ requires N, 13.21%.

Wallach's Transformation. 2 gm. of I were added to 100 c.c. of concentrated sulphuric acid. On gentle warming I dissolved readily in the acid with a yellowish colour. On heating further the solution turned a deep reddish brown. In a number of experiments these solutions were kept at 130° to 150°C . for 1 to 6 hours. In other instances the solution was kept at 100° for 12 to 24 hours. After cooling these solutions were poured into about 10 volumes of cold water and a yellow precipitate was obtained which could be recrystallised from anisole or alcohol. The melting point of the purified substance was found to be 284° and it was not depressed by admixture with a specimen of I. Furthermore the reaction product analysed for $\text{C}_{14}\text{H}_8\text{O}_9\text{N}_4$. All these observations indicated that the original substance I had not been materially altered by the treatment with sulphuric acid although it had retained a characteristic yellow colour after several recrystallisations. On dissolving it in alkali a red solution was obtained. On preparing the ethyl ester of I treated with sulphuric acid an ester was obtained which was also characterised by a darker colour and the formation of a reddish tint on the addition of alcoholic alkali. Otherwise it was found to be identical with the original ethyl ester of I. Therefore it was concluded that probably traces of the corresponding oxyazo compound had been formed, which, however, so far has not been isolated.

In applying more rigorous conditions in the attempt to bring about a Wallach's transformation, such as higher temperatures or longer periods of heating, far-reaching destruction of the molecule of I was found to occur.

Preparation of II. 2 gm. of I were added to 30 c.c. of concentrated nitric acid ($d = 1.48$) and the reaction mixture was heated with refluxing. After a few minutes a clear solution formed and dark brown fumes were evolved which contained a considerable amount of carbon dioxide. This was proved by testing the gases evolved, after bubbling them through water, with a solution of barium hydroxide. After boiling the reaction mixture for about 16 hours it was cooled and added to a large volume of ice water. An almost white granular precipitate (II) was obtained. Yield approximately 1.4 gm. M.P. approximately 210°C . After repeated recrystallisations from alcohol II was

obtained as practically colourless needles which melt at 216°C . It gave a colourless solution with sodium bicarbonate and carbonate solutions, indicating the presence of a carboxyl group. The colour of the solution of II in caustic alkali varies from colourless to deep red according to the concentration used. Strong caustic alkali, however, affects an alteration in the molecular structure of II, because on acidification a brown gelatinous compound is obtained which is not identical with II.

Found: C, 41.90; H, 1.84; N, 18.30%. $\text{C}_{13}\text{H}_7\text{O}_9\text{N}_5$ requires C, 41.38; H, 1.85; N, 18.56%.

Ammonium 3,5,3'-trinitro azoxybenzene 5' carboxylate. 1 g. of II was suspended in 20 c.c. of warm water. Concentrated ammonia solution was added drop by drop while the reaction mixture was vigorously shaken till the substance had gone into solution. A large excess of ammonia has to be avoided, otherwise the solution turns pink. On standing the ammonia salt of II crystallised out. After repeated recrystallisations from water it consisted of fine cream-coloured needles which lost their water of crystallisation *in vacuo* at 60°C . The colour of the anhydrous product was yellow.

Found: Total N, 21.1; ammonia N, 3.3%. $\text{C}_{13}\text{H}_{10}\text{O}_9\text{N}_6$ requires total N, 21.44; ammonia N, 3.55%.

Reaction of I and II with Acetone and other Methyl Ketones. A normal solution was prepared by dissolving 1.89 gm. of I in 10 ml. of N sodium hydroxide. To 1 ml. of an aqueous acetone solution was added 0.2 c.c. of the reagent and 0.5 ml. of 10 N sodium hydroxide. After standing for a few minutes a purple coloration occurred which increased on standing.

A similar colour reaction was obtained by the methyl and ethyl ester and caustic alkali of I and caustic alkali when added to a solution of alcohol containing acetone.

A number of other methyl ketones such as acetophenone, methyl ethyl ketone, ethyl acetoacetate, cyclohexanone and 2-methyl-cyclohexanone were tested and were found to yield a similar colour reaction with I.

If II was added to strong alkali *per se* a red colouration was obtained. However, no colour change was observed if II was dissolved in sodium carbonate solution or 0.1 N sodium hydroxide, and under these conditions a very strong purple coloration was obtained in the presence of acetone or other methyl ketones. The test was best executed by

adding 1 c.c. of a solution of II in sodium carbonate to 1 c.c. of an aqueous solution of acetone. Then 1 c.c. 0.1 N sodium hydroxide was added. Almost immediately a purple colour was obtained, which within a few minutes changed towards a red brown.

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THE AGE OF THE MARULAN BATHOLITH.

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

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The large outcrops of granitoid and porphyritic rocks occurring in the Marulan district were first examined and recorded by Woolnough.¹ Further investigation by various workers has shown that the extent of this intrusive mass is much larger than was previously supposed, the outcrop being from five to ten miles in width and from thirty to forty miles in length. The rock types are varied, including granites, granodiorites, dioritic and syenitic rocks, porphyries and porphyrites, but most have the appearance of being comagmatic. This view was held by Woolnough, and expressed more recently by Browne² in his account of palæozoic igneous activity. The last-named writer groups them with the Hartley and Bathurst granites, and tentatively assigns to them the same age, i.e. closing Upper Devonian. The present writer, in a paper published some years ago,³ while assuming that the Marulan Batholith was of post-Devonian age, was content in the absence of definite information concerning the relation between it and the Upper Devonian strata, to indicate it on his map as "post-Silurian".

At no place within the area studied by the writer up to that time had the igneous rock been found in contact with the Upper Devonian sediments, nor does it seem likely that such a contact does actually exist there. However, additional study in adjoining localities, both to the north and south, at Bannaby and Bungonia respectively, has provided the necessary evidence for assessing the age of the batholith within narrow limits.

¹ Woolnough, W. G. : The General Geology of Marulan and Tallong, N.S.W. *Proc. Linn. Soc. N.S.W.*, 1909, 34, 782.

² Browne, W. R. : Presidential Address. *Proc. Linn. Soc. N.S.W.*, 1929, 54, Part 1.

³ Note on the Geology of the Goulburn District, with Special Reference to Palæozoic Stratigraphy. *THIS JOURNAL*, 1935, 59, 75-85.

(a) Bannaby District.

Near the village of Bannaby, about twelve miles east of Taralga, at a height of nearly three thousand feet above sea level, there occurs a gently folded series of sandstones (quartzites) and conglomerates with subordinate slate. These rocks, or, more strictly, the arenaceous members, contain a great abundance of Upper Devonian marine fossils—a typical Lambian fauna. To the west they overlie Ordovician and Silurian strata, but on the eastern side they are in contact with a porphyritic rock representing a northerly extension of the Marulan batholith. The igneous rock is met with in the valleys and on the hillsides, but the tops of the hills are invariably capped with the Devonian strata. So far no actual exposure of the line of junction has been discovered, but it is possible almost everywhere* to determine its position to within a few feet.

Tracing this boundary for a distance of several miles it is found everywhere to conform to the dip of the overlying Devonian strata, and in no cases is the igneous rock found to transgress the normal line of the base of the sediments. The relation of outcrop to contour is entirely suggestive of the absence of any intrusive relationship, a conclusion which is supported by the fact that no contact metamorphic effects are exhibited by the Upper Devonian rocks. In fact, the conglomerates near the base of the series are so little affected even by regional metamorphism, and so nearly horizontal, that they might easily be mistaken in places for those of Kamilaroi age occurring about fifteen miles to the south-east. (The fossils, of course, are a sufficient indication of their real age.)

Another definite indication that the Devonian sediments were laid down upon an eroded surface of igneous rock is the presence of numerous pebbles of weathered porphyritic material in the conglomerates. On the whole, these conglomerates consist mainly of pebbles of quartzite (obviously derived from the Ordovician and Silurian strata to the westward) but in certain bands at least half of the pebbles are of igneous origin.

It is of interest to note that it is difficult, if not impossible, to find fresh specimens of porphyry for some distance below the base of the Devonian strata, suggesting extensive

* The exceptions are associated with heavy deposits of talus on steep slopes.

weathering of the igneous rock before the deposition of the sediments.

(b) Bungonia District.

A relatively restricted outcrop of Upper Devonian strata (with characteristic fauna) occurs a little to the south-west of Bungonia, along and to the west of the course of Bungonia and Lumley creeks. These rocks dip gently westward and are bounded on the east partly by a granitic phase of the Marulan batholith and partly by underlying Upper Silurian strata. As at Bannaby the boundary can be traced for some miles without any suggestion of intrusive characters, and the weathered granite, exposed in many places in the creek beds, is generally devoid of xenoliths. A small excavation made by the writer at a point a little south of the junction of Lumley and Bungonia creeks has exposed the actual junction between the Devonian rocks and the granite, which may thus be examined closely.

The basal beds of the Upper Devonian series are composed of a coarse gritty rock rather resembling a consolidated granite sand, containing feldspathic material cementing the quartz grains. Above these beds are conglomerates of relatively fine texture, the pebbles (mostly quartzite) being set in sandy matrix. One or two pebbles of igneous material have been noted, but as the batholith here is granitic one would not expect it to have survived intact in a subsequent formation to the same extent as it would have done where the dominant types are porphyritic and hence more resistant to weathering. This would appear to explain the difference between the Bannaby and Bungonia occurrences in this respect. Neither the sandstones, conglomerates, nor shales of the Devonian series show any signs of contact metamorphism although the limestone and shale of the Silurian series have been converted by the granite into marble and hornfels respectively.

CONCLUSION.

In the light of the foregoing descriptions it would appear that the Marulan batholith at its northern and southern extremities does not intrude the Upper Devonian, and, in view of the continuity and affinities of the various rock types throughout its extent, this may also be regarded as true of the middle region. On the other hand, there is undoubtedly evidence that it intrudes the Upper Silurian strata, as witness, for example, the wonderful array of

contact metamorphic rocks near the Marulan limestone quarry.

In assigning an age to this particular igneous intrusion, it may be said that it took place between the close of the Silurian period and the beginning of the Upper Devonian. It is to be noted that the porphyrites have been invaded and metamorphosed by the plutonic rocks. This, however, does not necessarily imply any great difference in age, and in view of the association of porphyries and porphyrites with granitic rocks in other parts of New South Wales and in Victoria it is probable that the granodiorite and porphyrite are comagmatic, as Woolnough contended. The Marulan mass is therefore to be regarded as a composite batholith, all components of which were injected during the same epoch of intrusion.

It is impossible as yet to say with certainty whether the batholith was actually emplaced before the beginning of the Devonian period ; but the component rocks do not show the tendency to gneissic or schistose structure which appears to be characteristic of epi-Silurian intrusions in other parts of the State.⁴ Dr. Ida Brown has shown that an important diastrophism occurred at the close of Middle Devonian time,⁵ and to this epoch the intrusion is most probably to be assigned.

⁴ Browne, W. R. : *Loc. cit.*

⁵ Brown, Ida A. : Late Middle Devonian Diastrophism in South-eastern Australia. *Proc. Linn. Soc. N.S.W.*, 1932, 57, 323.

STUDIES IN METAMORPHISM AND ASSIMILATION
IN THE COOMA DISTRICT OF NEW SOUTH
WALES.

PART I. THE AMPHIBOLITES AND THEIR METASOMATISM.

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(With four text-figures.)

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I. INTRODUCTION.

In his account of the general geology of the Cooma District W. R. Browne (1914)⁽³⁾ recorded a roughly circular mass of amphibolite, about 50 yards in diameter, in the town of Cooma 200 yards south of the R.C. church. Smaller masses, measuring a couple of yards in diameter, were recorded from the western end of the town on the Berridale Road, Por. 3, Par. of Cooma; from Pine Valley and from west of the Mittagong Road near the south-west corner of Por. 108, Par. of Binjura.

With the exception of the Pine Valley occurrence the amphibolite outcrops are completely surrounded by an

acid gneiss, termed by Dr. Browne the Cooma gneiss. Furthermore, it was noted that a coarse type of amphibolite, with interstitial white felspar, passed abruptly into finer grained types, and that the former was closely associated with intrusive pegmatite.

The relative ages of the amphibolite and Cooma gneiss, with its associated pegmatite, are rather obscure, as there are apparent contradictory lines of field evidence, and it was suggested in the 1914 paper that the relation between the amphibolite and pegmatite required laboratory investigation.

I should like to take this opportunity of thanking Dr. Browne for allowing me to undertake this work, for making available his specimens and field notes, and for his interest and helpful discussion during the progress of the investigation. To Mr. H. F. Whitworth, Curator of the Mining Museum, I am indebted for the loan of a specimen and slide of the Cooma amphibolite analysed by Mr. H. P. White.⁽¹⁹⁾ For financial assistance I gratefully acknowledge a grant from the Commonwealth Research Fund which is administered by the University of Sydney.

II. FIELD RELATIONS.

Reference to Dr. Browne's map will show that the country about Cooma is composed of Ordovician and Silurian rocks which are partly overlain by Tertiary basalts. The Ordovician series has suffered intense folding and the schists are injected by acid gneisses and associated pegmatites. Among the schists there is a hornblende-pyroxene-bearing type, and in a later communication it will be shown that this bears no relation to the amphibolites at present under discussion. The amphibolites, therefore, appear to be a distinct type, possibly representing a small intrusion which either antedated or postdated the Cooma gneiss.

On three occasions I have been to Cooma with geological parties led by Dr. Browne, so have had his field observations on the amphibolites pointed out to me. Recently I paid two further visits to the district and spent several days collecting and making a detailed study of the field relations in the small quarries on the south-western side of Soho Street between the intersections of Murray and Victoria Streets.

The following is a summary of the most important field observations that Dr. Browne and I have made on the amphibolites :

- (1) Close field relation between coarse amphibolite and pegmatite.
- (2) Numerous quartz-plagioclase veins cutting amphibolite and apparently related to pegmatite (see Fig. 1).
- (3) Coarse amphibolite not a homogeneous rock, but showing all gradations between a coarse hornblende-quartz-plagioclase rock with inclusions of fine amphibolite, and coarse hornblende-quartz-plagioclase veins threading fine amphibolite (see Fig. 2).

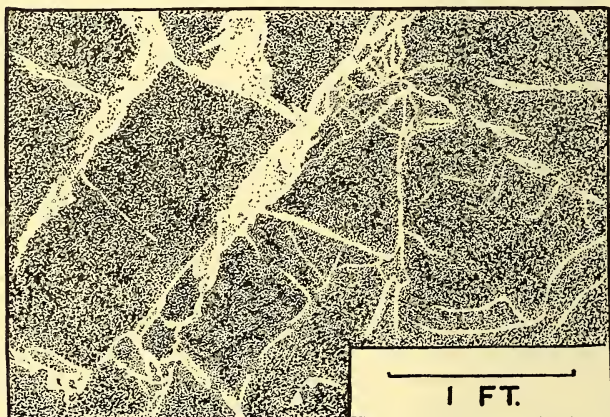


Fig. 1.—Quartz-plagioclase Veins cutting Amphibolite.
 Drawn from photograph by W. R. Browne.

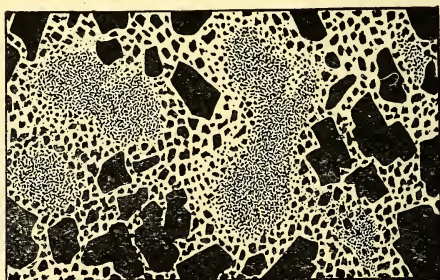


Fig. 2.—Drawing of Polished Surface of Heterogeneous Amphibolite.
 Natural size.

- (4) Coarse amphibolite apparently intrusive into fine type, and possibly into Cooma gneiss.
- (5) Occasional inclusions of amphibolite in gneiss.
- (6) Basification of gneiss in the vicinity of amphibolite suggested by the development of abundant biotite.

III. PROPOSED LINES OF INVESTIGATION.

To interpret the above field facts the following lines of laboratory investigation suggest themselves before the question of the age and origin of the amphibolite can be discussed.

- (1) To ascertain if there be any relation between the fine inclusions and the coarse veins in the heterogeneous type.
- (2) To investigate any relation between the fine amphibolite and the fine-grained inclusions in the heterogeneous rock.
- (3) To investigate any relation between the quartz-plagioclase veins and the hornblende-quartz-plagioclase veins of the heterogeneous amphibolite.
- (4) To ascertain if there be any relation between the pegmatite and the quartz-plagioclase veins.

In the following pages a detailed description of each rock-type is given with a view to establishing these relations.

IV. PETROGRAPHY.

(i) Amphibolites.

(a) Relict Gabbro.

In the hand specimen these are even medium grained rocks with a high density and very dark green colour. Under the microscope a relict structure indicates an igneous plutonic rock, with subidiomorphic prisms or irregular grains of plagioclase interspersed with groups of small crystals or granules of hornblende, diopside, epidote, and plagioclase, which suggest the recrystallisation of the larger crystals of a ferromagnesian mineral—possibly of augite.

The plagioclase prisms are about 1.5 mm. in length. Extinction measured on the albite twinning in sections normal to 010 is $35\frac{1}{2}^\circ$, $\alpha=1.561$ and $\gamma=1.570$. The composition is therefore basic labradorite ($Ab_{37}An_{63}$). The mineral is much saussuritised and sometimes shows alteration along cracks to an isotropic mineral which may be a chlorite.

Hornblende forms subidioblastic prisms (1 mm.) or small rounded grains (0.1 mm.) and inclusions of apatite

and sometimes of magnetite and sphene may be present. The hornblende is light yellowish-green in colour with $Z > Y > X$, $Z \wedge c = 22^\circ$, $\alpha = 1.643$, $\gamma = 1.660$.

Diopside is variable in amount, being very abundant in some types and absent in others. Like epidote, which is also rather sporadic in its development, the diopside always occurs in small rounded subidioblastic crystals or grains. Apatite is sometimes present in small stout prisms.

Large irregular grains of quartz are numerous, and these are either vein-like or interstitial in their occurrence, and may surround and isolate the plagioclase crystals. Sometimes small radiating filaments of quartz or minute strings of quartz beads are present in the plagioclase, suggesting a myrmekite-like⁽¹⁶⁾ replacement (see Fig. 3 (c)).

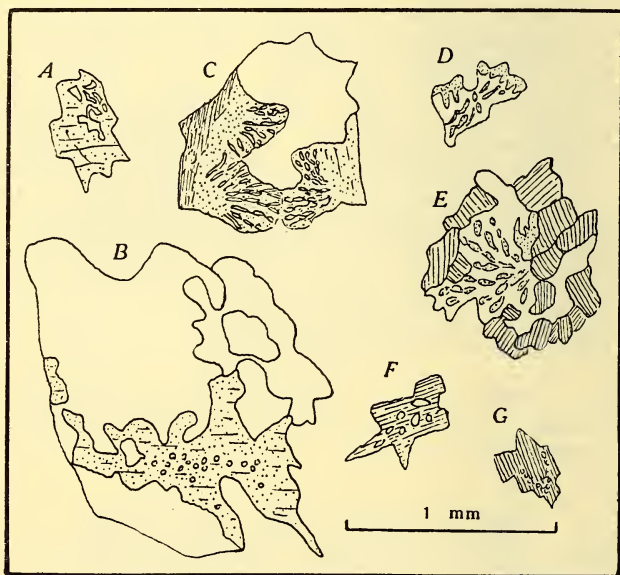


Fig. 3.

- A and B. Various stages in the replacement of labradorite by quartz. The quartz is attacking along cleavage planes in this type. (A) Labradorite with angular inclusions of quartz. (B) Large quartz grain enveloping resorbed angular skeleton of felspar.
- C, D and E. Myrmekite-like replacement of labradorite by quartz. (C) Filaments and beads of quartz in labradorite, surrounding large quartz grain which was possibly introduced by displacement. Note strain cracks in felspar on left. (D and E) Bead-like remnants of plagioclase surrounded by quartz.
- F and G. Hornblende crystals showing drop-like inclusions of quartz.

Although most of the quartz seems to have been introduced by replacement, small local areas of parallel cracks indicate strain and suggest that some displacement of the other minerals may have taken place. One rock contains interstitial micropegmatite, which points to the addition of a little orthoclase with the quartz.

A rather unusual rock has been analysed by Mr. H. P. White. This contains no quartz, large tabular subidiomorphic crystals and irregular grains of labradorite up to 3 mm. across, hornblende crystals averaging 1 mm., but occasionally attaining a size of 6 mm. and thus closely resembling the large hornblendes of the heterogeneous rock described on p. 93. The plagioclase shows slight alteration, but there is no evidence of recrystallisation or of silicification, and the rock appears to be a relict gabbro of somewhat coarser grain size than those mentioned above. The large crystals of hornblende may represent original hornblende crystals which have not been recrystallised, or, what seems more likely, they may have grown at a late stage in the rocks' history as a result of the concentration of volatiles along certain channels. The presence of these large hornblende crystals would place this rock among the heterogeneous types, but as it shows relict structures and differs from all the other heterogeneous rocks in the absence of quartz and acid plagioclase, it seems more fitting to describe it here. The analysis is given below, and, as no introduced material can be detected, it is assumed that this represents the composition of the original rock from which the amphibolite was derived.

SiO ₂	52.50
Al ₂ O ₃	11.72
Fe ₂ O ₃	2.30
FeO	5.94
MgO..	10.44
CaO	13.04
Na ₂ O	0.97
K ₂ O	0.53
H ₂ O +	1.66
H ₂ O -	0.28
TiO ₂	0.22
MnO	0.11
NiO . CoO	0.01
P ₂ O ₅	0.07
Cr ₂ O ₃	0.02
V ₂ O ₃	0.05
CO ₂	0.06
					<u>99.92</u>
Sp. Gr.	2.993

Relict gabbro (slightly heterogeneous). Behind Dodds' Hotel, Cooma.
Anal. H. P. White. *Ann. Rept. Dept. Mines*, 1909, 198.

(b) Even-grained Amphibolites.

In the hand specimen these rocks appear to be even-grained and both fine and medium types may be recognised, the latter closely resembling the relict gabbros. They are often intersected by quartz-plagioclase veins (see Fig. 1).

Under the microscope the even grainsize is not so apparent, and crystalloblastic structures are evident, the most common being a poikiloblastic development of plagioclase. The large (3-5 mm.) optically continuous sheets are quite clear and free from saussuritisation but enclose small granules or subidioblastic prisms of hornblende and often of diopside as well. The feldspar is sometimes untwinned but usually both albite and pericline twinning are developed. Extinction on the albite lamellæ in sections normal to 010 is 35° , $\alpha=1.560$ and $\gamma=1.570$, so the composition is basic labradorite ($\text{Ab}_{37}\text{An}_{63}$).

In the fine-grained amphibolites the ferromagnesian crystals measure about 0.15 mm. and in the medium-grained types the hornblende crystals vary from 0.5-1 mm. and may show a slight schiller-structure and a brownish core. The hornblende is optically negative with positive elongation, $Z \wedge c=22^\circ$, X =yellowish-green, Y =pale yellowish-green and Z =bluish green. Sphene is often present as inclusions in the hornblende, magnetite is conspicuous by its absence, and apatite, though rare, may be present in small stout prisms associated with quartz. Tiny flakes of biotite have been noted in the hornblende of a few rocks.

Quartz varies in amount and occurs interstitially or as ill-defined veins. Two types of replacement of plagioclase by quartz are shown. First, a myrmekite-like growth with fingers of quartz penetrating the feldspar, followed by a more advanced stage when only threads and beads of feldspar remain in a quartz host (see Fig. 3 (c), (d), (e)). Secondly, a replacement along cleavages, which first appears as a series of angular inclusions of quartz in basic feldspar resembling a micrographic intergrowth. This is followed by various stages, the most advanced showing rather angular skeletons of feldspar surrounded by large grains of quartz. At this stage the feldspar and the accompanying hornblende often contain drop-like inclusions of quartz (see Fig. 3 (a), (b), (f), (g)).

Some of the even-grained types have a granoblastic structure, but it is difficult to say whether this represents a true crystalloblastic structure or whether it is due to a partial replacement of poikiloblastic plagioclase by irregular

grains of quartz. Fine- (0.15 mm.) and medium-grained (1 mm.) granoblastic rocks occur, and in the hand specimen these cannot be distinguished from the poikiloblastic types.

Evidence of local strain is often shown by an alignment of the hornblende crystals and by a series of parallel cracks in the quartz and feldspar.

The following is an analysis of a fine-grained granoblastic rock, containing 10.44% of quartz and very little feldspar (see Fig. 4 (a)).

SiO ₂	59.13
Al ₂ O ₃	7.92
Fe ₂ O ₃	0.98
FeO	4.06
MgO..	14.29
CaO	12.37
Na ₂ O	0.44
K ₂ O	0.15
H ₂ O+	0.31
H ₂ O-	0.15
TiO ₂	0.32
P ₂ O ₅	abs.
MnO	0.10
Cr ₂ O ₃	tr.
					100.22
Sp. Gr.	3.039

Fine-grained granoblastic amphibolite containing 10.44% of quartz (found by Rosiwal measurement and calculated to wt. %). Anal. G. A. Joplin.

(c) Heterogeneous Amphibolites.

These rocks vary from fine-even-grained amphibolites veined by a coarse hornblende-quartz-plagioclase rock to coarse hornblende-quartz-plagioclase types with inclusions of fine amphibolite (see Fig. 2).

The fine patches are usually rounded and measure about $\frac{1}{2}$ inch across. They are similar to the fine amphibolites described above and may show either a poikiloblastic (see Fig. 4 (b)) or a granoblastic structure, the plagioclase showing varying degrees of replacement by quartz. The hornblende is optically identical with that of the even-grained rocks, and usually the plagioclase has the same composition (Ab₃₇An₆₃). In some rocks, however, a more acid variety of feldspar has been noted—Ab₄₀An₆₀ to Ab₅₀An₅₀. Diopside may or may not be present in the fine-grained inclusions. Magnetite is absent and apatite rare. A few of the heterogeneous rocks contain very basic



Fig. 4.

- A. Fine grained granoblastic amphibolite showing intergrowth of hornblende and quartz. A very small quantity of diopside and plagioclase is also present. $\times 10$.
- B. Heterogeneous amphibolite showing corner of large hornblende crystal surrounded by quartz and andesine and associated fine poikiloblastic type. The right-hand top corner consists of a single crystal of labradorite with small inclusions of hornblende and diopside. $\times 10$.

inclusions consisting almost exclusively of small (0.15 mm.) crystals of hornblende. The absence of both felspar and quartz suggests that only the felspar is being silicified.

The coarse phase of the heterogeneous rock consists of large subidioblastic crystals of hornblende, often over 7 mm. in length, adjacent to or partly surrounded by large grains of quartz and andesine ($Ab_{54}An_{46}$) with $\alpha=1.550$ and $\gamma=1.560$. Hornblende crystals of intermediate size (1-2 mm.) often occur between the large crystals and the fine inclusions (see Fig. 2), but this is not always the case and a large crystal of hornblende may be in direct contact with the fine type. A unique rock, which contains a few large crystals of hornblende and no quartz, has been described with the relict gabbros. The possible origin of this type will be discussed later (see p. 102).

The large hornblende crystals may have a slightly brownish core, but otherwise appear identical with the hornblende of the finer grained types. The hornblende from the coarse phase of a heterogeneous rock has been analysed, and a calculation based on Warren's formula⁽¹⁸⁾ shows that it is very rich in the tremolite-actinolite molecule,

with Fe/Mg 1/4·17. A small amount of aluminium replaces silicon in the tetrahedral chain and a comparable amount is present in the Y group. The mineral is negative with positive elongation, $Z \wedge c = 22^\circ$, $Z > Y \gg X$, with X=yellowish-green, Y=yellowish-green and Z=bluish-green, $\alpha = 1.643$, $\gamma = 1.660$ and $(\gamma - \alpha) = 0.017$.

		Wt. %		No. of metal atoms on basis of 24(O, OH, F).	
SiO ₂	..	50.08	..	7.15	} 8.00
Al ₂ O ₃	..	9.42	..	1.57	
TiO ₂	..	0.36	..	0.04	} 5.16
Fe ₂ O ₃	..	1.14	..	0.12	
MgO	..	16.00	..	3.42	} 2.15
FeO	..	6.89	..	0.82	
MnO	..	0.33	..	0.04	} 1.42
Na ₂ O	..	1.09	..	0.31	
CaO	..	12.53	..	1.81	} 1.42
K ₂ O	..	0.21	..	0.03	
H ₂ O	..	1.49	..	1.42	} 1.42
F	..	nd	..	—	
		99.54			
Sp. Gr.		3.119			
Anal. G. A. Joplin.					

The andesine associated with the large hornblende crystals often surrounds cores of corroded labradorite and may show a peculiar mottling which seems to indicate replacement by a more sodic feldspar.⁽⁶⁾ Apatite is often present in small stout crystals, and quartz, which is usually very abundant, occurs in large irregular grains. Occasionally the quartz is accompanied by granular epidote and in these types andesine is not abundant.

A type rich in quartz was crushed and the fine and coarse phases separated and analysed (see Table I, columns I, II). As there is no essential mineralogical difference between the phases except for a greater abundance of quartz in the coarse type, the analyses have been re-calculated on the basis of equal silica, and the close chemical relation is shown in columns III, IV below.

Special mention should be made here of a rock occurring at Pine Valley. It closely resembles the amphibolite, but consists chiefly of fibrous amphibole and chlorite. As it occurs among the schists, and appears to have suffered dynamic metamorphism, the discussion on this type will be reserved until the schists are further examined.

TABLE I.

	I.	II.	III.	IV.
SiO ₂ ..	52.06	62.12	51.73	51.73
Al ₂ O ₃ ..	14.83	10.51	14.75	13.47
Fe ₂ O ₃ ..	1.08	1.62	1.07	2.08
FeO ..	4.51	3.89	4.47	4.98
MgO ..	11.75	9.16	11.68	11.73
CaO ..	12.31	10.06	12.24	12.89
Na ₂ O ..	1.19	0.87	1.18	1.11
K ₂ O ..	0.98	0.61	0.97	0.78
H ₂ O+ ..	0.60	0.29	} 0.95	} 0.68
H ₂ O- ..	0.36	0.24		
TiO ₂ ..	0.29	0.32	0.29	0.41
MnO ..	0.67	0.11	0.67	0.14
P ₂ O ₅ ..	abs.	abs.	—	—
Cr ₂ O ₃ ..	tr.	tr.	—	—
	100.63	99.80	100.00	100.00
Sp. Gr. ..	3.100	2.821	—	—

I. Fine phase of Heterogeneous Amphibolite. Soho Street, Cooma. Anal. G. A. Joplin.

II. Coarse phase of Heterogeneous Amphibolite associated with fine phase of analysis I. Anal. G. A. Joplin.

III. Analysis I re-calculated to 100%.

IV. Analysis II re-calculated to 100% after deducting 10.39% of SiO₂.

(ii) Quartz-plagioclase Veins.

These veins (see Fig. 1) intersect all types of the amphibolite. Occasionally narrow strips of the amphibolite are isolated between two parallel veins or rifted off by converging ones. In the small strip-like rafts of heterogeneous amphibolite both coarse and fine phases may be identified. The veins are white in colour; the larger ones are a couple of inches in width but the majority are about $\frac{1}{2}$ inch across. They appear to be intimately related to the pegmatite dykes which are adjacent to the amphibolite, but the exact relation cannot be satisfactorily determined in the field. That is, no vein can be actually traced from the pegmatite, nor can the dyke be seen cutting the smaller veins.

Under the microscope the veins are seen to consist almost exclusively of the three minerals—quartz, plagioclase and apatite. The relative abundance of quartz and felspar varies greatly, and many of the veins consist almost entirely of quartz. Hornblende and labradorite sometimes occur as xenocrysts, and there is sometimes a slight suggestion that some of the hornblende may have crystallised from solution. The plagioclase is very variable in composition, independent crystals and borders around labradorite xenocrysts ranging from andesine ($\text{Ab}_{64}\text{An}_{36}$) to oligoclase ($\text{Ab}_{72}\text{An}_{28}$).

In most cases the margin of the vein is quite sharp against the invaded rock, but occasionally poikilitic plates of andesine occur in the amphibolite adjacent to the vein, and, except for their more sodic nature, might easily be mistaken for the poikiloblastic crystals in the metamorphosed basic rocks.

(iii) Tourmaline Pegmatite Dykes.

The largest of the pegmatite dykes have been mapped by Dr. Browne,⁽³⁾ who has also given an account of their field occurrence and macroscopic characters. In the vicinity of the Soho Street quarries the dykes are a couple of feet in width, with the outer part consisting of a coarse graphic intergrowth of quartz and felspar and passing inwardly into a zone rich in felspar with a rude comb-structure. A few large crystals of biotite and of tourmaline may be present in this zone, and the centre of the dyke is infilled with quartz, sometimes associated with large crystals of tourmaline.

Under the microscope the felspar proves to be microcline-micropertthite. Although albite is apparently intergrown with the microcline, the potash felspar shows evidence of albitisation, suggesting that soda-rich solutions were active towards the close of crystallisation.

V. NATURE OF THE ORIGINAL BASIC ROCK.

The foregoing petrographical descriptions and chemical analyses indicate that the amphibolites have suffered silicification, and that the coarse heterogeneous types differ from the even-grained only in that they usually contain more quartz and often a more sodic felspar, indicating a late introduction of albite. There is abundant evidence to show that much of the silicification was a replacement process, and it is of interest to note that some of the

structures observed in the partly silicified labradorite are comparable to structures noted in metalliferous replacements (Bateman,⁽²⁾ Anderson,⁽¹⁾ and Schouten⁽¹⁵⁾). Nevertheless, the occasional vein-like occurrence of the quartz in the less replaced rocks, and sometimes the local areas of strain, suggest that some of the quartz may have been introduced by displacement.

As the relict gabbro, whose analysis is quoted on p. 91, contains neither quartz nor acid felspar, it is assumed that it represents the composition of the original rock. Furthermore, the fine inclusions analysed from the heterogeneous rock contain very little introduced material, and, although they have been recrystallised, it is unlikely that they have changed much in composition. Reference to the other analyses, however, show that these rocks, on account of the metasomatic processes, possess very unusual chemical characters, with comparatively high silica, lime and magnesia, and low alumina. In considering the origin of the rocks, therefore, it is necessary to make allowance for the material which has passed in and out of the system. It was shown in Table I that the coarse phase of the heterogeneous rock differed from the fine phase only in its greater amount of quartz, and that the two rocks were chemically similar when re-calculated on an equal silica basis. It was thus tacitly assumed that the quartz had been introduced by displacement, although such an assumption is not entirely justified. With regard to the fine even-grained amphibolite there is abundant evidence to show that much of the felspar has been replaced by quartz, although some of the quartz may have been introduced by displacement. For the purpose of re-calculating the analysis on the most accurate basis possible, Rosiwal measurements were made to ascertain the amount of quartz present and the weight percentage was found to be 10.44%. On account of the possibility of some displacement it could not be assumed that there was a volume for volume replacement of felspar by quartz; so after 10.44% of SiO_2 had been deducted sufficient labradorite ($\text{Ab}_{37}\text{An}_{63}$) was added to make the silica percentage equal to that of the relict gabbro, and the whole analysis was re-calculated to 100%.

Although much has been assumed in re-calculating these analyses there is good petrographical evidence for the assumptions that have been made, and reference to Table II will show that the rocks show a consanguinity which was

TABLE 2.

	I.	II.	III.	IV.	V.	VI.	VII.
SiO ₂ ..	52.50	52.06	51.73	52.50	48.91	51.50	52.00
Al ₂ O ₃ ..	11.72	14.83	13.47	10.86	8.81	10.89	11.59
Fe ₂ O ₃ ..	2.30	1.08	2.08	1.04	1.04	1.75	2.72
FeO ..	5.94	4.51	4.98	4.34	9.52	6.86	7.18
MgO ..	10.44	11.75	11.73	15.29	15.19	13.91	12.87
CaO ..	13.04	12.31	12.89	14.05	14.69	10.19	10.49
Na ₂ O ..	0.97	1.19	1.11	0.82	0.64	1.18	1.06
K ₂ O ..	0.53	0.98	0.78	0.16	0.10	0.24	0.92
H ₂ O+ ..	1.66	0.60	0.37	0.33	0.52	2.40	0.37
H ₂ O- ..	0.28	0.36	0.31	0.16	0.07	—	0.18
TiO ₂ ..	0.22	0.29	0.41	0.34	0.37	0.20	0.99
P ₂ O ₅ ..	0.07	abs.	abs.	abs.	tr.	tr.	tr.
MnO ..	0.11	0.67	0.41	0.11	0.16	tr.	tr.
Etc. ..	0.14	—	—	—	0.15	0.76	0.04
	99.92	100.63	100.00	100.00	100.17	99.86	100.41

- I. Relict gabbro (slightly heterogeneous), Cooma. Anal. H. P. White.
- II. Fine phase of Heterogeneous Amphibolite. Cooma. Anal. G. A. Joplin.
- III. Coarse phase of Heterogeneous Amphibolite, Cooma. Re-calculated as explained above.
- IV. Even-grained Amphibolite re-calculated to 100% after deducting 10.44% of quartz and adding 7.07% of labradorite as explained above.
- V. Olivine gabbro (IV.1.2.2.2), Orange Grove, Baltimore Co., Maryland. Anal. W. F. Hillebrand. G. H. Williams, *U.S. Geol. Surv. Ann. Rept.*, 15, 674, 1895. In W.T. No. 7, p. 709.
- VI. Diorite (III.5.4.(4)5), Mazaruni River, British Guiana. Anal. J. B. Harrison. J. B. Harrison, *Goldf. Bri. Gui.*, 49, 1908. In W.T. No. 65, p. 647.
- VII. Norite (III.5.4.(3)4), Cow Creek, near Bridger Peak, Wyoming. Anal. E. T. Allen. H. C. Spencer, *U.S. Geol. Surv. Prof. Paper*, 25, 32, 1904. In W.T. No. 46, p. 645.

not so apparent before. Moreover, they are now comparable with other normal basic rocks. These rocks are all characterised by low alumina and high magnesia, and the Cooma rocks are particularly rich in lime. This suggests the former presence of olivine and/or hypersthene, and possibly of diopsidic pyroxene. On whatever basis the analyses may be re-calculated, it is obvious that II and III

were slightly more aluminous than the other Cooma rocks and that IV was a slightly more melanocratic type; thus there appears to have been some differentiation in the original rock mass, which possibly consisted of norites and olivine gabbros. The presence of relict structures confirms this supposition.

VI. METAMORPHIC HISTORY OF THE AMPHIBOLITE MASS.

It has been shown that the amphibolite mass consists of relict gabbros, fine and medium even-grained amphibolites and coarse grained heterogeneous amphibolites, and that the whole mass is invaded by small quartz-plagioclase veins and by a dyke of granite pegmatite. Furthermore, it has been shown that the original rock, from which all types of amphibolite were derived, was of the nature of a gabbro or norite.

The various metamorphic processes which brought about the change from gabbro to amphibolite will now be considered, and it will be shown that the development of the present amphibolite mass, with its several types, took place in a number of stages:

- (a) By contact metamorphism.
- (b) By metasomatism involving replacement of the felspar by quartz.
- (c) By albitisation and further silicification of the felspar accompanied by a simultaneous increase in the size of the hornblende crystals, and sometimes by a deposition of epidote.
- (d) Finally by the injection of small quartz-plagioclase veins.

(a) The development of poikiloblastic and granoblastic structures and the reduction of grainsize (Tilley,⁽¹⁷⁾ Joplin,⁽⁷⁾ Grout⁽⁵⁾) in the amphibolites indicate an initial thermal metamorphism of the gabbro, which no doubt was due to the intrusion of the Cooma gneiss. No foliation appears to have accompanied this metamorphism, although the enveloping acid rock has a primary gneissic structure. That the amount of amphibole so greatly exceeds pyroxene suggests that the metamorphism was a medium grade "wet" type.

Evidence of relict igneous structures in the gabbro indicates that the basic rocks had not been stressed before the thermal metamorphism took place, and it seems evident that the gabbro was intruded before the folding

or before it reached its maximum. The maximum possibly synchronised with the intrusion of the Cooma gneiss, and the solid gabbro was partly suspended in the acid magma as a roof-pendant; so was thus protected and remained unstressed.

(b) At this stage, however, the gabbro was subjected to intensive silicification and the greater part of the basic felspar was dissolved and stored up in the aqueous solutions which were the agents of metasomatism. The exact nature of these solutions is unknown, but it is evident that they contained large volumes of silica, and that at a later stage soda became concentrated; thus aqueous siliceous and waterglass solutions are indicated. It is possible that some of the ferromagnesian minerals may have been removed also, but there is very little petrographical evidence for this. The completeness of the silicification of the felspar in many of the rocks points to the maintenance of a fairly high temperature and concentration of these solutions over a long period.

(c) The formation of the heterogeneous rock appears to have occurred at a slightly later stage than the silicification of the even-grained amphibolites and possibly after the complete solidification of the enveloping gneiss and the intrusion of the pegmatite. It has been pointed out that the microcline of the pegmatite has been albitised, and, although albite solutions were becoming sufficiently concentrated to be precipitated in the heterogeneous amphibolite, it is likely that the albitisation of the pegmatite belongs to a later period. The felspar of the heterogeneous amphibolites is andesine and acid labradorite of somewhat variable composition. Some of this plagioclase was no doubt deposited from solution, the potential albite having been basified by the anorthite-molecules that had been stored up in the liquid. The more basic types of felspar, however, represent the reaction between these solutions and the solid labradorite. Read and Phemister^{(11) (12)} have pointed out that albite solutions cannot react with a lime-rich basic rock to give a more calcic felspar unless sufficient alumina be available. In the case of the Cooma rocks the anorthite molecule must have been available either in solid labradorite or in solution after its replacement by quartz. Epidote was no doubt formed by the addition of lime to this anorthite-molecule, the lime having been released by the amphibolisation of the pyroxene.

The development of the large hornblende crystals is rather difficult to explain. Some of the medium grained rocks show a slight indication of the growth of hornblendes, and here it appears to have taken place in the solid and to be a metamorphic phenomenon. The very large crystals of the heterogeneous rock, however, are usually adjacent to large crystals of quartz or andesine; and apatite is usually present in stout crystals. Their growth thus appears to have been promoted by volatiles.

The chemical composition of the hornblende indicates that it is a metamorphic rather than an igneous type,⁽⁸⁾ and this is further suggested by its similarity to the hornblende of the metamorphosed even-grained amphibolites. Therefore, the large crystals cannot have crystallised from solution, but may have formed as the result of the coalescence of the small hornblende inclusions in the felspar porphyroblasts that have been replaced by quartz and more sodic felspar. Volatiles have promoted this coalescence, which was not possible during the earlier stage of silica replacement owing to an insufficient concentration of volatiles. Read⁽¹¹⁾ in describing the Ach'uaine hybrids notes a similar development of large hornblende crystals in and along the margins of intrusive felspathic veins, and Deer⁽⁴⁾ records large porphyroblasts of hornblende at the contact of granite and hornblende-schist "especially in proximity to the narrow permeating veins of volatile-rich emanations from the granite". The association of quartz and acid plagioclase with the large hornblende crystals is to some extent fortuitous and occurs only because these more acid minerals were being precipitated when volatiles are sufficiently concentrated to promote the growth of the hornblende. In the case of a heterogeneous relict gabbro (see p. 89) neither quartz nor acid felspar are associated with the large hornblende crystals, but their abnormal growth is nevertheless probably due to the escape of volatiles along sinuous channels in the rock-mass. A similar development of large hornblende crystals along cracks where volatiles were escaping was observed in a hybrid hornblende-gabbro at Hartley. At Hartley, as at Cooma, the large hornblende crystals occur in vein-like segregations, and, although Grout⁽⁵⁾ criticises the use of the term "segregation" with regard to a hybrid rock, there seems to be no other way of describing or accounting for these vein-like occurrences.

(d) As the quartz-plagioclase veins usually show a sharp contact with all types of amphibolite, they belong to a still later period. Their felspar is more sodic than that of the coarse phase of the heterogeneous rock, which would indicate a greater enrichment of albite in the invading solutions. These veins seem to be connected with a late stage in the crystallisation of the adjacent pegmatite, the microcline of which is partly albitised; though the onset of albitisation possibly synchronised with the formation of the heterogeneous amphibolite. The pegmatite dykes were probably intruded at about the time of the initial silicification of the gabbro, and the presence of a little micropegmatite in one of these rocks further points to this period. Moreover, the pegmatite dykes are in general parallel to the grain of the country and were evidently injected before the decline of shearing stress, although crystallisation took place after compression had ceased. The small quartz-felspar veins are neither orientated nor ptygmatic and suggest a state of tension rather than of compression.

VII. AGE OF THE AMPHIBOLITES.

In tabulating the field relations it was recorded that there were some apparent contradictions regarding the relative ages of the amphibolite and Cooma gneiss. These, however, may be explained.

The basification of the gneiss near the amphibolite and the presence of basic inclusions in the acid rock indicate that the amphibole antedates the gneiss. Moreover, it has been shown that the basic rock has been metamorphosed and metasomatised by the gneiss. Whether the gabbro represents an earlier crystallisation phase of the granite magma, or whether it is of still earlier origin is impossible to ascertain.

The evidence for its post-gneissic age was based on the apparent close association with the pegmatite and a possible intrusive relation against the gneiss. These observations apply to the coarse amphibolite which has resulted from emanations derived at a late stage from the acid magma. This type would therefore post-date the gneiss; thus the observed facts would be explained.

VIII. COMPARISON WITH SIMILAR ROCKS ELSEWHERE.

Heterogeneous hornblendic rocks containing quartz and alkaline felspar have been described from various parts of

Scotland and from Ireland. Their origin has been variously ascribed to fractional crystallisation accompanied by filter-press action,⁽⁹⁾ to the assimilation of quartzite xenoliths by an ultrabasic magma^{(13) (14)} and to reaction between quartz-felspar solutions derived from an acid magma and a solid ultrabasic rock.^{(11) (12)}

So far as the Cooma rocks are concerned the explanation of differentiation accompanied by pressure is quite untenable. First, there is evidence of metamorphism in the amphibolite pre-dating the formation of the heterogeneous rock; in the second place the rocks have obviously been silicified; thirdly the hornblende is not an ordinary igneous variety; and, finally, when the heterogeneous rocks were formed they were probably in a state of tension, whereas filter-press action requires compressional forces.

Regarding the explanation put forward by Miss Reynolds⁽¹³⁾ it must be admitted that the enveloping gneiss at Cooma contains many inclusions of quartzite and quartz-schist, and it is possible that the earlier intrusion of gabbro may have picked up similar inclusions. Nevertheless, careful search has not revealed any trace of such xenoliths. At Colonsay the transfusion of quartzite, poor in alkalis, has caused an enrichment of potash, which is precipitated as orthoclase in the appinite. At Cooma, however, no orthoclase has been noted and only a silica and soda enrichment occurs. Moreover, the country rocks which form the xenoliths in the Cooma gneiss usually contain a high percentage of biotite, which would tend to bring about a potash enrichment in the contaminated rock. The absence of potash felspar in the Cooma amphibolite and its presence in the associated pegmatite excludes this rock from being the leucocratic end-member of a transfusion process. Furthermore, the bulk of pegmatite as compared with amphibolite, and the association of gneiss and pegmatite in regions where amphibolite is absent, make such a suggestion quite untenable. If the small quartz-plagioclase veins are to be regarded as the final products of transfusion, then it must be borne in mind that most of the end-members of the gneissic magma have suffered albitisation.

It is believed that the heterogeneous rocks at Cooma were formed by the action of granitic or trondhjemitic emanations on a gabbroid rock, an explanation very similar to that put forward by Read to account for the Ach'uaine hybrids.

Read and Phemister⁽¹²⁾ and MacGregor and Kennedy⁽¹⁰⁾ have suggested a correlation between the Ach'uaire hybrids of Sutherland and the appinites of the west coast of Scotland. Though these authors were agreed that mineralogically and texturally the rocks are very similar, they hold very different views regarding their origin.

There seems to be reliable field evidence for each of the explanations put forward concerning the origin of these heterogeneous hornblendic rocks, and the question arises, can a rock of similar mineral composition and fabric be formed in different ways? The answer surely appears to be in the affirmative, and it would seem that these rocks are not a unique type, but may be formed under a variety of physical and chemical conditions. The complex and variable nature of hornblende itself favours such a suggestion, and the fact that it occurs in both igneous and metamorphic rocks of very diverse composition would necessarily make it a common mineral. Moreover, quartz and alkaline felspar (both albite and orthoclase) are ubiquitous minerals, which are stable over a wide range of physical conditions, and these minerals are frequently precipitated at a time when volatiles are concentrated and when physical conditions favour the growth of hornblende crystals.

IX. SUMMARY.

It has been shown that the Cooma amphibolites have a very simple mineral composition and consist almost entirely of hornblende, plagioclase and quartz. Even-grained and heterogeneous types occur, the latter consisting of the even-grained type cut by hornblende-quartz-plagioclase veins, which have originated by reaction between the original basic rock and late solutions from the adjacent gneiss and pegmatite. The amphibolites have suffered recrystallisation and intense silicification, and when due allowance is made for these processes it is evident that the original rock was a gabbro or norite which was intruded before the gneiss.

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THE CONSTRUCTION OF A QUARTIC SURFACE
WITH TWO DOUBLE LINES AND FOUR
TROPES.

By L. S. GODDARD, B.Sc.

Communicated by PROFESSOR T. G. ROOM, M.A.

(With Plate II and four text-figures.)

(Manuscript received, June 21, 1939. Read, July 5, 1939.)

Models of surfaces possessing interesting geometrical properties are not very common and for demonstration purposes a model was constructed, which illustrates some of the properties of surfaces dealt with in the geometrical theory. The surface to be described was chosen because of the following features :

- (i) It lies entirely within a sphere.
- (ii) It possesses
 - (a) two double lines,
 - (b) four tropes,
 - (c) synclastic and anticlastic parts,
 - (d) a simple parabolic curve.

These are all easily visible.

The surface has for its equation

$$x^2y^2+z^2(x^2+y^2+z^2-c^2)=0 \dots\dots\dots (1)$$

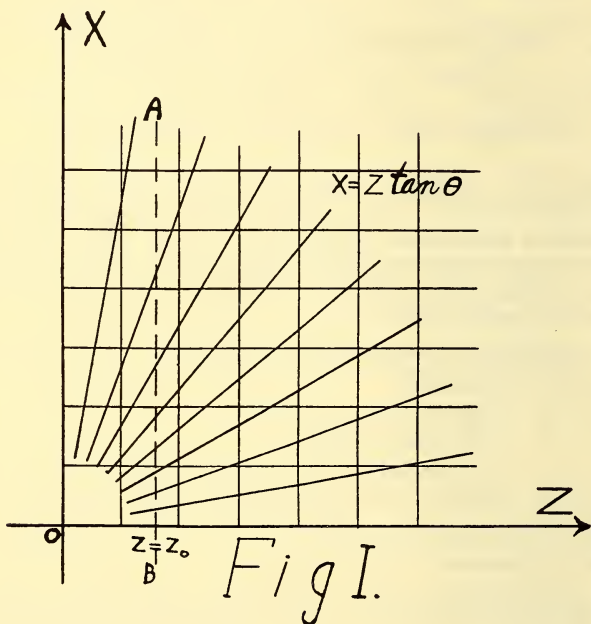
and, to make the model a convenient size, the value of c was chosen to be three inches. Then the complete model fits within a sphere of radius three inches. To construct the surface the contour lines $z=\text{constant}$ were drawn for various values of z advancing by $\frac{1}{4}$ inch from zero to three inches. These were drawn on a piece of five-ply wood, $\frac{1}{4}$ inch thick, and the sections of the surface were cut out and glued together. Finally the surface was made smooth and continuous by suitable filing and sandpapering.

A good deal of calculation would normally be required to draw the curves $z=\text{constant}$ for a general surface; but the special form of equation (1) allows us to use a graphical method involving straight lines and circles, and this reduces the labour of calculation considerably.

Equation (1) may be derived from the following two equations by the elimination of θ :

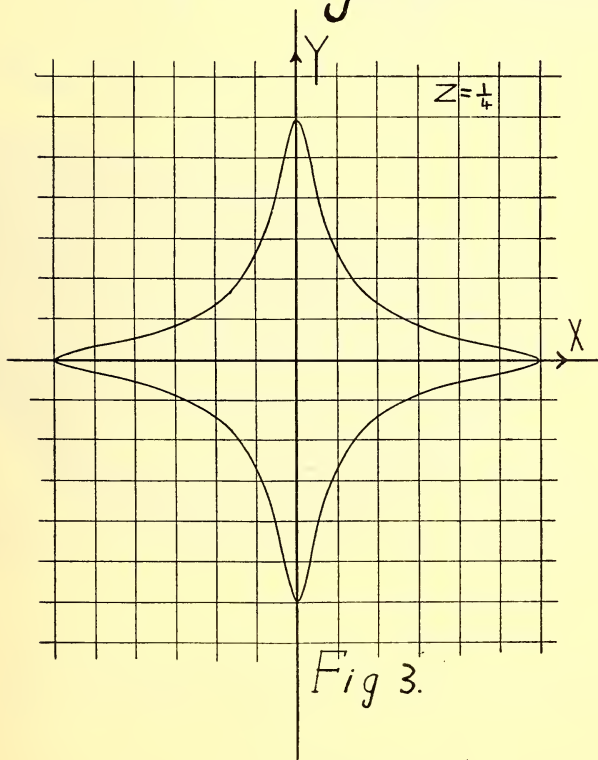
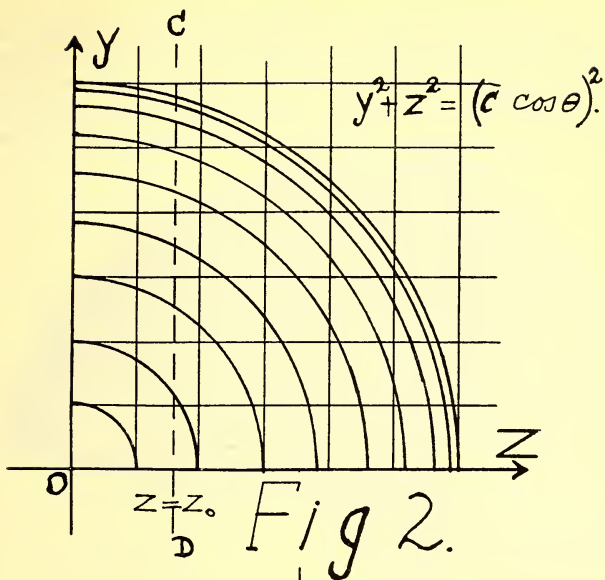
$$\begin{aligned}x &= z \tan \theta \\ y^2 + z^2 &= (c \cos \theta)^2.\end{aligned}$$

Thus the series of lines $x = z \tan \theta$ may be drawn for various values of θ as in Fig. 1, and the corresponding series of circles $y^2 + z^2 = (c \cos \theta)^2$ as in Fig. 2.



To draw the section of the surface by $z = z_0$, draw the dotted line $z = z_0$ to cut the above series of right lines and circles. Now place Fig. 1 on the (x, y) plane so that BA coincides with the x -axis and then prick through the points where BA cuts the series of lines. Then with Fig. 2 on the (x, y) plane so that DC coincides with the y -axis, prick through the points where DC cuts the series of circles. Now corresponding values of x and y are plotted, providing a series of points on the graph.

The sections are symmetrical about the axes of x and y and also the lines $y = \pm x$. Thus only one-eighth of the



contour need be plotted. In Fig. 3 and Fig. 4 are shown the contours for $z=\frac{1}{4}$ inch and $z=2$ inches respectively.

To investigate the properties of the surface we observe, firstly, that the lines $x=0, z=0$ and $y=0, z=0$ are each double lines on the surface. The equation (1) can be written in the parametric form

$$x=c \sin \theta \sin \varphi$$

$$y=c \cos \theta \cos \varphi$$

$$z=c \cos \theta \sin \varphi.$$

We find for the total curvature¹ the value

$$K=c^{-2}(\cos^2 \theta - \cos^2 \varphi)(\cos^2 \theta - \sin^2 \varphi \cos^2 \varphi)^{-2}.$$

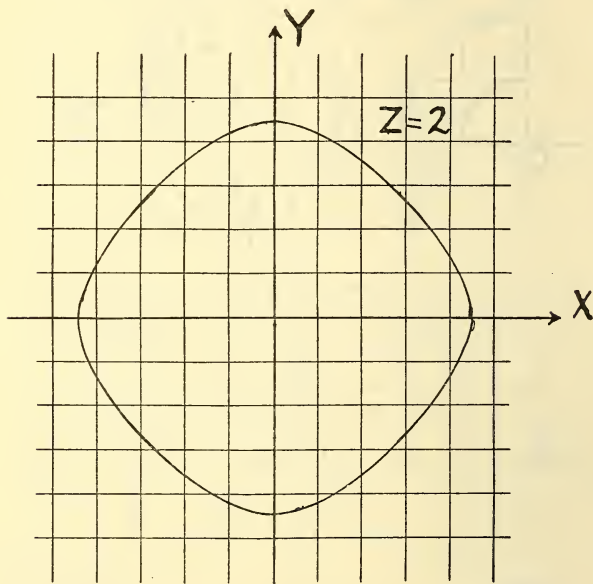


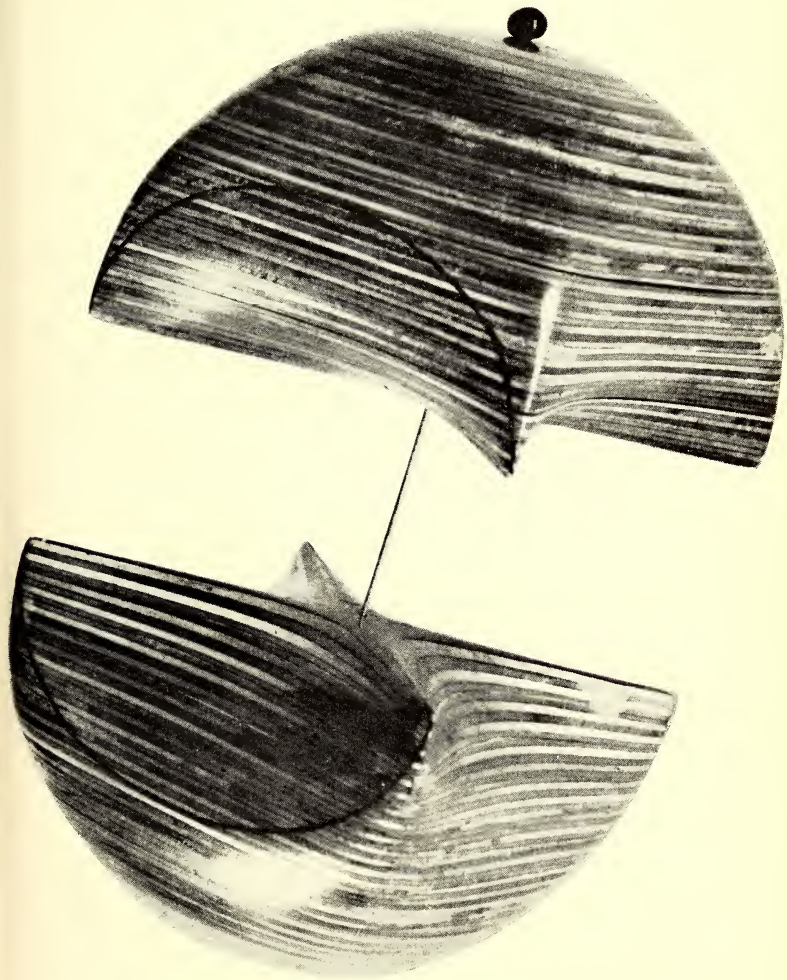
Fig 4.

For points at which the surface is synclastic $K > 0$ (e.g. the ellipsoidal surface), and for points where the surface is anticlastic $K < 0$ (e.g. a saddleback surface). The parabolic curve separates these two parts and for it, therefore, $K = 0$, i.e.

$$\cos^2 \theta = \cos^2 \varphi$$

$$\text{or } \theta = \pm \varphi, \pi \pm \varphi.$$

¹ Weatherburn : Diff. Geom., Vol. I (Cambridge, 1927), p. 69.



Thus the curve consists of four parts given by

$$\left. \begin{aligned} x &= \pm c \sin^2 \theta \\ y &= \pm c \cos^2 \theta \\ z &= \pm c \sin \theta \cos \theta \end{aligned} \right\} \text{ and } \begin{aligned} x &= \mp c \sin^2 \theta \\ y &= \pm c \cos^2 \theta \\ z &= \mp c \sin \theta \cos \theta. \end{aligned}$$

These four parts are curves lying in the four planes $x \pm y = \pm c$. Moreover each of these four planes touches the surface along the curve and is thus a trope. For example $x + y = c$ cuts the surface in a curve which satisfies

$$x^2 y^2 + z^2 (z^2 - 2xy) = 0$$

i.e. $(xy - z^2)^2 = 0$.

Thus the curve is the intersection of the plane $x + y = c$ with the cone $xy - z^2 = 0$, and is therefore an ellipse whose orthogonal projection on to the x -plane or the y -plane is a circle. The complete parabolic curve consists of four such ellipses lying one in each of the four planes $x \pm y = \pm c$.

ACKNOWLEDGMENT.

In conclusion I wish to thank Professor T. G. Room for the help and advice he has given throughout this work; also Mr. K. R. M. Hart, Department of Mechanical Engineering, who photographed the model. Part of the above work was carried out during the tenure of a Sydney University Science Research Scholarship.

EXPLANATION OF PLATE II.

Model of the surface $x^2 y^2 - z^2 (z^2 + y^2 + x^2 - c^2) = 0$, cut through the plane of the two double lines, the halves separated to show the shape of the surface. The black line on the surface is an ellipse forming part of the parabolic curve. The part of the surface inside the ellipse is anticlastic and the part outside is synclastic.

INFRA-RED RADIATIONS WITH SPECIAL
REFERENCE TO THEIR QUENCHING
EFFECTS UPON ZINC SULPHIDE
PHOSPHORS.

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(Communicated by Professor O. U. VONWILLER.)

(With Plates III-V.)

(Manuscript received, June 21, 1939. Read, July 5, 1939.)

Much work has been done in study of fluorescence and phosphorescence. Already a number of books have been written on the subject.¹ Consequently the author is able to quote only a few necessary historical facts having special reference to this work, before describing his own contribution to the subject.

HISTORICAL.

Fluorescence and Phosphorescence.

Many important facts and theoretical considerations were recorded at a discussion on luminescence by members of the Faraday Society at Oxford in October, 1938²; fluorescence and phosphorescence were defined (for practical purposes) as follows:

A, B, C, Plate III, Fig. 1, is a time curve of luminescence. A substance may be said to be "fluorescing" whilst it is being subjected to an exciting radiation. As soon as the exciting radiation is removed, the luminescence of the substance commences to decrease as depicted from B to C, and during this period the substance may be said to be "phosphorescing".

¹ Handbuch der Experimentalphysik, Band XXIII, by P. Lenard, E. Schmidt and R. Tomaschek, "Phosphoreszenz-Fluoreszenz", Leipzig, 1928; "The Evolution of Forces", by Gustave Le Bon (Kegan Paul, Trench, Trübner & Co.), 1908; "Fluorescence and Phosphorescence", by Hirschclaff (Methuen & Co., London), 1938.

² *Faraday Society Transactions*, 35, 1-240, 1939, also *Science Abstracts*, February 25, 1939, 42, No. 679, 161-163, also *Nature*, 142, 1938, 779.

It was pointed out by N. Riehl that, in addition to the "phosphorescence" which is strongly affected by temperature and can be "frozen", there is an accompanying "afterglow" which is uninfluenced by temperature. Whilst "phosphorescence" can be increased only to the limit of "saturation excitation" afterglow can be increased practically without limit by increasing the exciting radiation. When the afterglow has died out there remains a certain amount of residual energy which can be stored up for any length of time until it is liberated by heat. This energy corresponds to phosphorescence.

Since the early investigations of E. Becquerel with his phosphoroscope, and of P. Lenard, a great deal of work has been carried out. Copious references are given in *Handbuch der Experimental Physik* (see ¹). In this work the effect of temperature on phosphorescence has been dealt with very fully. In this connection particular reference should be made to the work of F. Schmidt in 1920, who, amongst many other things, investigated the effect of changing the temperature of a phosphor whilst it was under illumination from a Nernst lamp.

Much information on the chemical side will also be found in these two volumes *re* the preparation of zinc sulphide phosphors³ and phosphors containing selenium. The effects of magnetic and electric fields also have been studied.

Becquerel and others have shown that a large number of phosphors have only a momentary duration of phosphorescence.

According to Le Bon (¹ "The Evolution of Forces") at a temperature below 0° C. varying with different substances, a body does not visibly phosphoresce. As the temperature rises, up to about 100° C., phosphorescent intensity increases. Above this temperature it decreases and reaches zero at about 500° C.

The same authority gives the following general law: "After a certain emission of light at a given temperature a phosphor indefinitely retains a *residual phosphorescence* as long as its temperature is not raised again."

³ See also "Zinc Sulphide Phosphors", *J. Chem. Phys.*, 6, 454-461, 1938, which deals with the theory of phosphorescence and copper-activated phosphors, also *J. Chem. Phys.*, 7, 4-7, 1939.

According to Houston⁴ *fluorescence* is explained on Bohr's theory as follows: "If, when an atom is raised to a higher state by absorption of light, it returns to the normal state by stages emitting light, in the process fluorescence takes place. Owing to the nature of the process, the emitted frequencies must be smaller than the absorbed frequency in accordance with Stokes' law."

THE WORK OF THE AUTHOR.

The present paper deals only with some effects observed with zinc and calcium, sulphide phosphors.

Phosphorescent Screens.

In order to study their properties, screens were prepared first as described by Le Bon.¹ The Zn S or Ca S was ground in a mortar and then passed through a fine silk sieve; finally it was mixed with bronzing varnish, the proportion of the phosphor being not less than 30%. After thoroughly mixing, it was poured (without being allowed to settle) on to a sheet of cardboard or glass laid flat. Screens made in this way dried and were ready for use in about fifteen minutes.

These screens answered fairly well, but did not phosphoresce so brilliantly as the original phosphors from which they were made.

It was next decided to employ a solution consisting of equal parts of amyl acetate and acetone, in which was dissolved sufficient celluloid to give it the viscosity of a thick varnish. Thoroughly powdered zinc sulphide or calcium sulphide was mixed into this and the mixture was poured on to cardboard or glass in similar manner to the bronzing varnish mixture of Le Bon. It dried in about the same time, and was found to possess a considerable increase of luminosity.*

The two following symbols are freely employed by the author for convenience of denotation. \odot Zn S denotes that a zinc sulphide screen at ambient temperature has not been exposed to exciting radiations, i.e. that it is not phosphor-

⁴ "Treatise on Light", by A. A. Houston. (Longmans, Green & Co.), 1938.

* It should be possible under pressure, or in some other manner, to manufacture a far more perfect screen, having a glazed surface similar to the calcium tungstate intensifying screens used in radiography. With a really well-finished screen, far more brilliant photographic results could be obtained.

escing; ✕ Zn S denotes that the screen at ambient temperature has been exposed to exciting light radiations and is phosphorescing.

Photographic impressions (contact prints) from phosphorescing screens are spoken of as *phosphorographs*.

Fluorescent Screens.

Fluorescent screens have been in use for radiography for many years. Röntgen first employed screens of barium platinocyanide for visual X-ray examinations, and the now general employment of "intensifying screens" when taking radiographs is due to a suggestion made by A. A. Campbell Swinton.⁵

A screen of calcium tungstate or other fluorescent material is placed in contact with an X-ray plate or film between the latter and the X-ray tube. The X-rays having penetrated the subject, cause the intensifying screen to fluoresce with an actinic light to which the plate is at least ten times more sensitive than it is to the X-rays. All intensifying screens make use of the part of the curve of luminescence between A and B, Pl. III, Fig. 1, and every endeavour is made to reduce phosphorescence to a minimum

In order to obtain photographic records of the effects of various visible and infra-red radiations upon a phosphorescent screen, Le Bon and others have made contact prints by placing a photographic plate in contact with the ✕ screen for a few seconds after the required visible effect has been obtained and while the screen is still phosphorescing.

The Quenching of Fluorescence by Infra-red Radiation in the Region A to B, Pl. III, Fig. 1.

The author has found that the quenching effects of infra-red rays are far less apparent during fluorescence than they are after the exciting radiation has been removed and phosphorescent decay has commenced. Phosphorographs A and B, Plate V, each show the images of the filaments of two 100 W. incandescent metal filament electric lamps. (see also Pl. III, Fig. 2.)

⁵ *Jour. Roy. Soc. Arts*, 44, 1896. At this lecture, Campbell Swinton said, "It appears to me that the sensitiveness of photographic plates to these rays might very probably be very largely increased by treating them with fluorescent materials or even arranging a fluorescent screen to be in contact with the film during exposure."

A Zn S Cu screen (green fluorescence) was first energized by an exposure of 10 seconds to a 500 W. D.C. arc between steel electrodes ; it was then placed in the position shown in Fig. 2 and the images of the two filaments F and F¹ were simultaneously projected on to it.

The light from L¹ was filtered by means of a trough containing cupric ammonium sulphate so that only blue rays were transmitted. The image of the lamp, therefore, increases the phosphorescence of the screen and shows as a bright line, B, on Pl. V, phosphorographs A and B.

The light from the other lantern was filtered by means of a sheet of black glass which cut out all visible radiations and transmitted only infra-red. These latter radiations quenched the phosphorescence of the screen and show as dark lines, Q, in the phosphorographs.

By increasing the intensity of the quenching radiations or by reducing the intensity of the blue energizing rays (by the employment of a diaphragm, additional blue filters, or a series resistance R) control was obtained of the effects produced on the Zn S screen—either the energizing or the quenching radiations were made to predominate at will. In phosphorograph A, Pl. V, blue radiations predominate, and in phosphorograph B of the same Plate quenching radiations are the stronger (note specially the point of intersection of the two filament images).

Plate III, Fig. 3 illustrates another experiment to show this effect ; in this case a transparent ✕ Zn S Cu screen (glass backing in lieu of cardboard) was employed.

The diffused blue rays from lamp L cause it to fluoresce weakly. As soon as the quenching rays from lamp L¹ are simultaneously projected on to the other side of the screen the fluorescence is extinguished (where the projected image of lamp L¹ falls upon the screen). The extinguishing action of infra-red rays upon fluorescence is comparatively weak, but as soon as the exciting radiations are removed and phosphorescence has commenced the quenching effects are relatively powerful.

The Quenching of Phosphorescence by Infra-red Radiations in the Region B to C, Pl. III, Fig. 1.

Pl. V, phosphorograph C, is a contact print from a ✕ Zn S Cu screen (green) on a panchromatic plate. The screen was first energized by an exposure of 10 seconds to a 500 W. D.C. arc. A strip of tinfoil, N, having a circular hole at its centre, was laid across it. Both screen

and foil were then covered by 24 thicknesses of thin black paper (selected) and placed near to a 100 W. incandescent metal filament electric lamp. When the black paper was removed from the screen (in the dark) the phosphorescence of the latter had been quenched everywhere except where it was shielded by the tinfoil, thus showing the transparency of the paper to infra-red radiations and the powerful extinguishing action of the latter in the region of the phosphorescent decay curve B and C, Pl. III, Fig. 1.

Chromatic Aberration and Astigmatism.

The employment of a ∇ Zn S screen in place of an ordinary photographic plate reveals defects not seen on the latter.

The general scheme of this experiment can be obtained by reference to Pl. III, Fig. 2; in this case, however, only one lamp, L^1 , was employed. Its light was unfiltered and the image of the filament was focussed through lens Y^1 on to a flat surface S. (Y^1 was set at an angle to the rays as indicated by the dotted line Y^2). First an ordinary photographic plate was placed at S and a rapid exposure given. The photographic image obtained is seen in photograph D, Pl. V.

A ∇ Zn S screen was then placed at S and another exposure was made; see the contact print (or phosphorograph) made from the screen after this exposure (upon a panchromatic plate), phosphorograph E, Pl. V. D and E are similar to F and G, but in the latter cases a diaphragm was employed covering $\frac{1}{2}$ of the lens Y^1 .

At the bottom of phosphorographs E and G the visible rays have caused increased phosphorescence and are at sharper focus (owing to the glass lens having different refractive indices for visible and infra-red radiations) than the quenching radiations which have given us the black lines on either side of the white phosphorescent line. In the absence of any visible rays the quenching effect would show up as a broad line covering the whole of the space occupied by the narrow and sharper focussed line of phosphorescence.

As the experiment was performed during fluorescence the unfiltered visible rays from the lamp were able to overcome the quenching completely. Reference to Pl. V, phosphorographs A and B, will show by the absence of dark shadows on either side of the filament image that the

filter employed had entirely absorbed the quenching radiations.

On the left-hand side of phosphorographs E and G, Pl. V, it will be observed that quenching has taken place only on the left-hand side of the filament image. This indicates that the lens is astigmatic; it has bent the visible rays towards the right in the vertical plane, whereas in the horizontal plane it has acted symmetrically.

Comparison of the Relative Focal Length of a Glass Lens to Blue and to Quenching Infra-red Radiations.

The light from a 100 W. metal filament lamp L, Pl. III, Fig. 4, was first scattered by means of a sheet of frosted glass placed between it and a narrow slit. On the other side of the slit filters of black and of blue glass were employed each covering half of the slit as depicted.

By means of a glass lens Y, the image of the blue half of the slit was brought to a sharp focus at position A on to a \times Zn S Cu screen (green). H, Pl. V, is a phosphorograph of the effect produced.

The screen was then re-energized and moved further from the lens until the quenching radiations gave a sharply defined image of the slit. Phosphorograph I, Pl. V, shows the effect produced.

A comparison of phosphorographs H and I shows that (1) when the blue rays were in focus, although the quenching rays were out of focus, they *were not scattered appreciably*; (2) whereas, when the quenching rays were in focus, the blue rays were not only out of focus but also were scattered strongly. A comparison of phosphorograph H with the filtered blue image of the filament seen in A and B, Pl. V, shows that the blue glass used in our present experiment was an imperfect filter and allowed the quenching radiations to operate on each side of the blue image of the slit. In order to bring the quenching rays to a sharp focus, the screen had to be moved approximately $2\frac{1}{32}$ inches further from the lens.

Given the refraction index of the latter and an accurate optical bench, it should be possible to calculate the wavelength of the quenching rays.

Scattering.

Further comparative tests of the scattering of visible and infra-red radiations were made as follows :

(1) A ✕ Zn S screen (Pl. III, Fig. 5) was placed in the shadow of a lip or shield P. Normally using a blue glass filter the light from lamp L was sufficiently scattered by a sheet of ground glass that it caused an increase in the brilliance of the phosphorescence of the screen.

(2) Still retaining the blue glass filter, when the frosted glass was removed the blue rays passed right over the Zn S screen and did not affect it.

(3) Using a black glass filter instead of the blue and leaving the frosted glass in position, it was not possible to obtain any evidence of scattering of the infra-red radiations.

(4) Evidence of scattering was obtained however in the following manner :

Pl. III, Fig. 2. The image of an incandescent lamp filament was projected by infra-red radiation through a black glass filter on to a ✕ Zn S (green) screen. Brightly burnished thin sheet ebonite, or clear glass, could be placed in any position in the path of the rays without destroying the definition of the image, but unpolished ebonite or ground glass dispersed the image unless placed in contact with the ✕ Zn S screen.

A Reversal of Image Effect and its Interpretation.

Phosphorographs J and K, Pl. V, show the effects of a small heating unit, illustrated in Pl. III, Fig. 6, upon a ✕ Zn S screen.

The heater coil R was enclosed within a metal shield M and when heated to about 45° C. it was placed in contact with the back of a ✕ Zn S screen (on cardboard).

The latter phosphoresced more brightly under the action of the heat, but a few seconds after the heater had been removed the bright patch (seen on phosphorograph J) gradually disappeared, and, as one watched, a dark patch gradually developed in its place (see phosphorograph K, Pl. V). This effect must not be confused with the well-known phenomenon of "photographic reversal". A certain definite amount of energy was stored within the zinc sulphide during its energizing exposure to light. Under normal conditions a certain amount of this energy would be gradually dispersed as phosphorescent light, following a decay curve as shown from B to C, Pl. III, Fig. 1. The effect of the heat has been to sharpen and

shorten this curve, i.e. energy was expended more rapidly, hence the increase of luminosity. This was followed on cooling by a deficiency of phosphorescence as compared with the rest of the screen, whose phosphorescence was decaying at its normal speed, and on the duration of the decay curve.

Phosphorograph L, Plate V, shows the speeded decay of luminescence, due to placing a small coin straight from one's pocket, at body heat about 36° C. (only 14.25 degrees above ambient temperature) on to the surface of a \times Zn S screen (green).

The Earliest Appearance of Quenching Radiations.

The heater unit F illustrated in Pl. III, Fig. 7 controlled by a variable series resistance R was fitted in an open-ended metal cylinder E, and the latter was fitted with a cardboard cover C, in the end of which was an orifice D. This was pushed over the cylinder until the cardboard end almost touched the heater coil. A \times Zn S screen (green) was then placed tightly against D and the heater coil was gradually raised in temperature from room temperature through dark heat to white heat. As the temperature increased the fluorescent image of the orifice grew in luminosity, but as soon as the heater reached a barely visible red heat (about 400° C.) quenching set in, which steadily increased in intensity with additional rise in temperature until the heater fused.

Another experiment was made in the following manner: The image of a bunsen gas flame was projected by means of a lens upon a \times Zn S screen (green). No quenching was observed, but after the introduction of a short length of iron wire into the flame, quenching occurred along the image of the wire as soon as the latter glowed at dull red heat.

Shift of Spectral Distribution Effect.

Pl. III, Fig. 8 represents a 100 W. metal filament electric lamp L controlled by means of a variable series resistance R. This was first set with its sliding contact at a position B, and a \odot Zn S screen (green) was exposed to the unfiltered light from lamp L at this setting. The \times Zn S screen thus energized was then covered with a sheet of metal provided with a small slit as shown in the figure.

The slider was then moved back to a position A and another exposure was given through the slit at this new

setting. This resulted in a quenching of the phosphorescence. The slit was then moved across to another part of the ✕ screen, and the slider of the resistance was moved to a position C, thus increasing the brightness of the lamp, and another exposure was made. This time an increase of luminosity resulted. The phosphorograph M, Pl. V, is a contact-print on a panchromatic plate from a ✕ Zn S screen after the three foregoing exposures.

The position B of the slider could be chosen at random at any point along the resistance; an increase of current through the lamp (i.e. an increase of filament temperature) always caused increased luminosity, whilst a decrease always caused quenching.

That this effect was due to a shift of spectral distribution and not to an alteration of light-intensity was shown as follows: Having energized the screen at any selected setting of the resistance, the former was removed to a greater distance from the lamp L. In this way we obviously decreased the intensity of the light according to the inverse square law but no quenching action occurred.

Infra-Red Radiographs.

Le Bon¹ showed that printer's ink is very opaque to infra-red radiations. He wrapped a printed sketch in black paper, placed it in an envelope in an ebonite box and obtained a good impression of the sketch upon a ✕ Zn S screen by means of the quenching radiations from a paraffin lamp.

N, Pl. V, is an infra-red radiograph taken in this manner of a newspaper cutting wrapped in black paper (selected) within an ordinary white paper envelope. The whole packet was opaque to visible light, but when it was placed upon a ✕ Zn S (green) screen and exposed to the quenching radiations from an ordinary otherwise unscreened 100 W. incandescent electric lamp for 10 seconds, the infra-red rays passed right through the packet as X-rays pass through an opaque body, and quenched the screen in varying degree in accordance with its varying densities. The ink being almost entirely opaque, prevented all quenching.

The phosphorograph N, Pl. V, here reproduced is a contact-print on a panchromatic plate from a ✕ Zn S screen after such a radiographic exposure.

A New Photographic Process.

(Positive and Negative Photographic Phosphorescent Impressions on Screens.)

Further consideration of the "shift of spectral distribution effect" showed that we had here a method of obtaining at will either a photographic positive or negative.

Phosphorographs.

Experiments were made and it was found that an ordinary finished photographic negative could be imprinted upon a Zn S screen. O and P, Pl. V, are a positive and a negative photograph respectively. Both are contact-prints on panchromatic plates made from phosphorescent impressions on Zn S screens.

In one case a finished negative was placed in contact with a \odot Zn S screen and an exposure was made to the light of a 100 W. metal filament electric lamp, and in the other case a \times Zn S screen was employed in contact with the same finished photographic negative and an exposure was made to the same lamp, but this time the visible radiation was filtered out by the employment of a thin sheet of ebonite.

Control of Contrast.

By making use of the "shift of spectral distribution" (see Pl. III, Fig. 8) we can obtain complete control of contrast, the greater the distance we move our sliding contact away from point B on either side, the greater will be the contrast obtained in printing from any negative. Contrast is also enhanced by the employment of filters.

Intensification by Heat.

By reference to Pl. V, phosphorograph JK, it is seen that heat increased the brilliance of the phosphorescence at the loss of its duration.

Phosphorograph Q, Pl. V, is a contact-print from a purposely under-exposed phosphorescent picture on a \times Zn S screen. The central portion has been intensified by heat. The procedure was as follows.

After a \odot Zn S screen covered by a finished photographic negative had been (under) exposed to a weak blue light, and had imprinted upon it a weak phosphorescent print, a short strip of copper heated to 45° C. was placed underneath and in contact with it, as depicted. As soon as the brilliance of the picture had increased to the required

degree, a contact print was made by placing a panchromatic plate on to the screen while it was still on the hot metal plate. This method is applicable, of course, whether one is making a positive or a negative print.

A Spectrographic Comparison of Zn S and Ca S Phosphors.

Pl. IV is the result of a spectrographic examination showing in which parts of the spectrum fluorescence commences and where quenching ends. Langley has shown that infra-red radiation extends from 0.4μ to beyond 7μ .

There is no need to dwell upon this as Langley, Le Bon and others have already made similar spectrographic investigations. It is interesting to note that Zn S (green) commences to fluoresce just on the green side of the F spectral line. Zn S (yellow) commences to fluoresce well down in the yellow, and Ca S commences to fluoresce in the purple end of blue.

The spectrograph employed was one manufactured by Griffin & Tatlock, in which the spectrum was obtained by means of a 6 V. incandescent electric lamp and a defraction grating. A sheet of red glass transparent to the quenching radiations was employed as a screen, to filter out the otherwise interfering secondary spectrum.

The wave-lengths of the phosphorescent light appear to be very sharply defined.

The Selective Properties of Zn S Phosphors.

A screen was made containing Zn S, green and yellow mixed in equal proportions. It was placed in front of the spectrograph and when viewed in the dark the selectivity of the phosphors was apparent. At the blue end of the spectrum only the Zn S (green) crystals were phosphorescing, whereas at the yellow end yellow phosphorescence was seen.

The experiment was also carried out in another way. A \odot 50/50 green and yellow Zn S screen was exposed to an electric light, one half being covered by a green glass filter and the other by blue glass. On removal of the filters in the dark, where covered by the blue glass it was phosphorescing with green light, and under the green glass the phosphorescence was yellow.

In another experiment a sheet of red glass was placed over a brightly phosphorescing Zn S screen (green). This completely cut out all visible radiations.

A test was made to see if the phosphorescence of one ✕ Zn S screen could be transmitted to another by contact; but the result was negative, both in the case of green to green, green to yellow, and *vice versa*, or yellow to yellow and yellow to green and *vice versa*.

Depth of Phosphorescence.

A tube was filled with powdered crystals of Zn S (green) and its open end was closed by a thin skin of celluloid dissolved in amyl acetate and acetone. When dry this end of the tube was exposed to light; it phosphoresced brilliantly, but as expected the phosphorescence was only on the surface. Apparently only the crystals actually exposed to the exciting radiation became luminous.

Fluorescence Preceding Quenching.

Working at a temperature of 19° C., it was observed that when the image of the filament of an electric lamp was projected by infra-red rays through a black glass filter on to a ✕ Zn S screen, in the case of Zn S (yellow) the quenching was very obviously preceded by a short period of increased luminosity. In the case of ✕ Zn S-Cu (green) the same effect was present, but it was more difficult to observe. The author found that it could be seen best if the Zn S screen was kept in slow motion. These and other similar investigations are still proceeding.

ACKNOWLEDGMENTS.

In conclusion the author wishes to express his thanks to Professor O. U. Vonwiller and members of the staff of the Physics Department of Sydney University for the helpful facilities they have afforded during these investigations, which have been made, for the most part, in the Physical Laboratories.

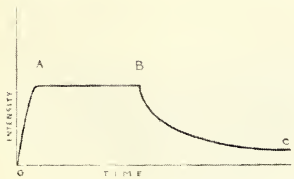


FIG 1



FIG 2.

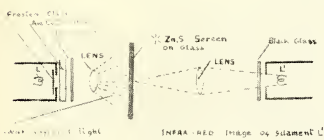


FIG 3.



FIG 4



P is a lip or chuck which puts the ZnS screen in shadow when the ground glass is removed

FIG 5.

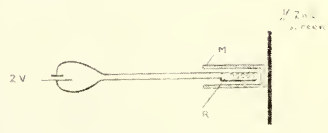


FIG 6

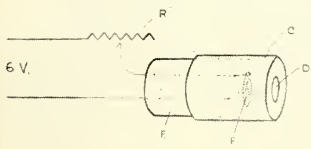


FIG 7. Diagram of Eureka wire and its holder E (1932)

FIG 7.

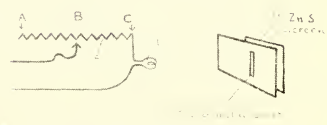
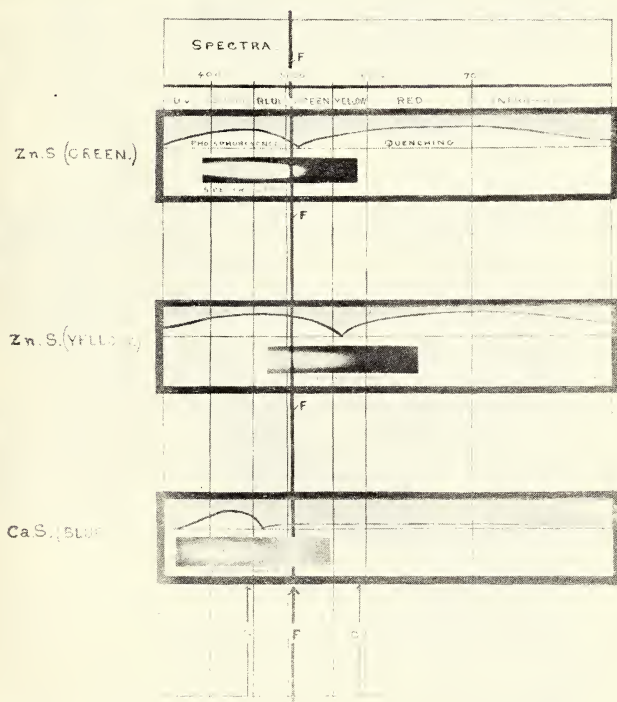
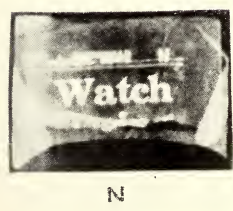
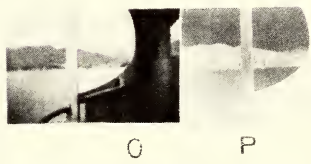
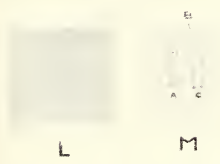
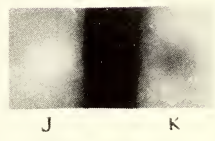
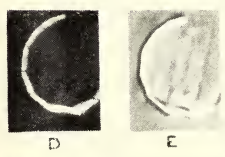
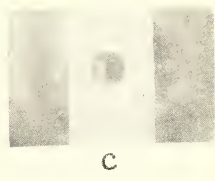
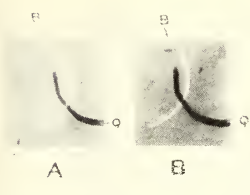


FIG 8





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NEW SOUTH WALES

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OF

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1939

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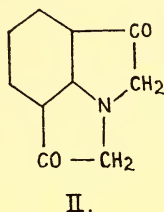
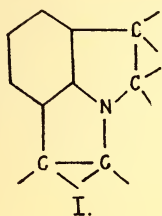
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A CONTRIBUTION TO THE STEREOCHEMISTRY
OF TERVALENT NITROGEN.By FRANCIS LIONS, B.Sc., Ph.D.,
and ERNEST RITCHIE, M.Sc.*(Manuscript received, June 23, 1939. Read, August 2, 1939.)*

Reference was made by the authors in a previous paper* to a suggestion put forward by Jackson and Kenner (*J.C.S.*, 1928, 573) that positive evidence for a planar distribution of the nitrogen valencies in a tervalent nitrogen compound in which three separate groups are attached to the nitrogen atom would be supplied "by the preparation of a compound in the molecule of which a nitrogen atom is common to two ring structures, which are at the same time plane and co-planar". Jackson and Kenner continued their argument as follows: "Since, so far as we know, there is no evidence available which renders doubtful the plane configuration of five-membered ring structures it would appear that these conditions would be fulfilled by a structure of type (I), if Kekulé's formula for benzene and its derivatives be accepted."

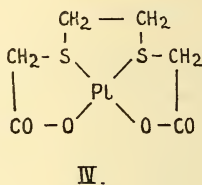
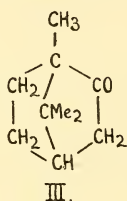


Jackson and Kenner attempted the preparation of the substance represented by formula (II); but although they were able to isolate a small amount of material of the expected composition, their result must be considered as inconclusive—as they themselves state.

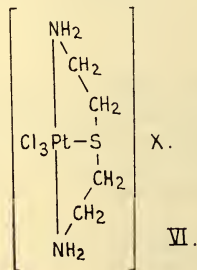
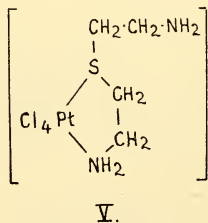
* Researches on Indoles. Part VII. By G. K. Hughes, F. Lions and E. Ritchie, *THIS JOURNAL*, 1938-39, 72, 209.

L—August 2, 1939.

Since the X-ray studies of Mrs. Lonsdale (*Proc. Roy. Soc., A*, 1929, 123, 494) have clearly indicated that atoms attached to the carbon atoms of a benzene nucleus lie in the plane of that nucleus, it does seem more than probable that structures of type (I) will be plane. On the other hand it must be pointed out that there are many substances known containing five-membered rings which are definitely not planar. Thus, the stable camphor (III) molecule contains two such puckered five-membered rings.

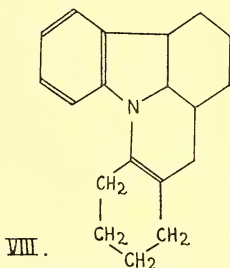
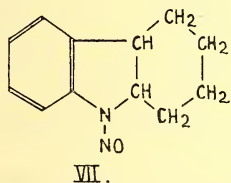


Also, the demonstration by Mills and Quibell (*J.C.S.*, 1935, 839) that the four valencies of the platinum atom in its 4-co-valent compounds all lie in the same plane, together with the recognition that 3-co-valent sulphur atoms have always a non-planar distribution of the sulphur valencies, necessitates a non-planar arrangement of at least one of the five-membered rings in the molecule of ethylene *bis* thioglycollato platinum (Ramberg and Tiberg, *Berichte*, 1911, 47, 733). It is probable that the five-membered ring containing the platinum atom and both sulphur atoms is buckled. In this connection it is significant that Mann (*J.C.S.*, 1930, 1745) was able to prepare and resolve the compound (V) in which the asymmetry of the molecule resides in the sulphur atom; and that he could prepare only one isomer of compounds of type (VI)—in which, owing to the spatial demands of

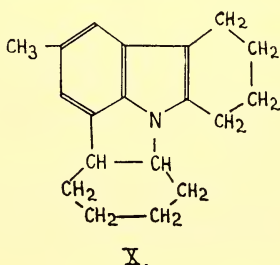
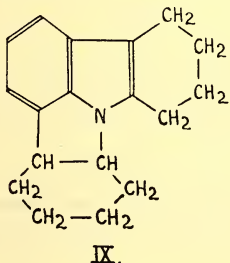


the 3-covalent sulphur atom, the $-NH_2$ groups most probably do not occupy trans positions in the co-ordination complex. Such an arrangement would necessitate the three sulphur covalencies lying in one plane.

Shortly before the publication of Jackson and Kenner's paper, there had appeared in the *Journal of the Indian Chemical Society* (1927, 4, 271) an account of several experiments by Manjunath which included the reduction in presence of cyclohexanone by zinc dust and acetic acid of 9-nitrosohexahydrocarbazole (VII) and the preparation by this method of a crystalline substance $C_{18}H_{21}N$, which Manjunath designated "8 : 9-(1 : 2-cyclohexyl) tetrahydrocarbazole", and to which he assigned the obviously incorrect structural formula (VIII) (which corresponds to $C_{19}H_{23}N$).



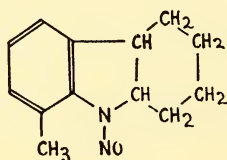
There seemed little doubt that Manjunath intended his structural formula to be (IX) [8 : 9-(1 : 2-cyclohexylene)-tetrahydrocarbazole], with which his name almost agrees, and which corresponds to the product to be expected if a normal Fischer indole ring closure had occurred. The properties of the substance also appeared to be in harmony with this formula (IX). A similar product (X) was obtained by Manjunath in somewhat less pure condition from 6-methyl-9-nitrosohexahydrocarbazole.



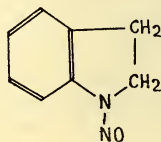
The substances (IX) and (X) contain the basic structure (I), postulated by Jackson and Kenner as fulfilling the requirements for planar distribution of the three nitrogen valencies: Because of the theoretical importance of (IX) we have repeated Manjunath's experiments with the nitroso derivative of cis-hexahydrocarbazole (*cf.* Gurney, Plant and Perkin, *J.C.S.*, 1927, 2676), and have confirmed his experimental result, although the product $C_{18}H_{21}N$ we were able to isolate had slightly different constants from those described by Manjunath, and we were unable to prepare a picrate from it at all.

We have also prepared 8-methyl-hexahydrocarbazole, which readily formed a nitroso derivative (XI). After reduction with zinc dust and acetic acid of this substance in presence of cyclohexanone, followed by warming, it was not found possible to isolate any substance other than a little 8-methyl tetrahydrocarbazole, formed, as shown later, by the pyrolysis during distillation of some unchanged 8-methyl-9-nitrosohexahydrocarbazole. The blocking of the 8-position in the hexahydrocarbazole nucleus by a substituent methyl group effectively prevents formation of a substance similar to (IX), and this failure is evidence supporting the structure (IX) assigned to Manjunath's compound.

More conclusive evidence, however, is to be found in the experimentally ascertained fact that reduction of 1-nitroso-indoline (XII) in presence of cyclohexanone with zinc dust and acetic acid leads readily to formation of a crystalline neutral substance $C_{14}H_{15}N$ melting at 154° .



XI.

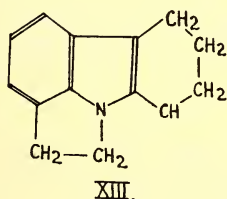


XII.

There can be no doubt that this substance is 8:9-ethylene-1:2:3:4-tetrahydrocarbazole (XIII), in which again the requirements specified by Jackson and Kenner are fulfilled.

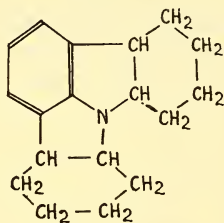
The authors are strongly of the opinion that in this substance the three nitrogen valencies are co-planar, but the possibility must not be overlooked that the carbon atom of the ethylene bridge attached to the nitrogen atom

might lie above or below the plane containing at the same time the benzene and pyrrole nuclei and the three atoms directly attached to the benzene ring. Such a non-planar configuration would involve some measure of strain in the reduced pyrrole ring, which would tend to oppose any tendency towards the non-planar distribution of the nitrogen valencies. It must be conceded that the failure to resolve suitable 3-covalent nitrogen compounds is evidence of marked dissimilarity between 3-covalent nitrogen and 3-covalent sulphur, the rigid non-planar distribution of the sulphur atom valencies contrasting strongly with the indefinite direction demands of the trivalent nitrogen atom—which suggests a planar distribution of the nitrogen valencies in (XIII) rather than a strained “puckered” ring.

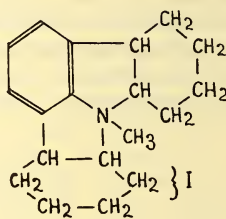


It is unfortunate that X-ray studies of the spatial arrangement of the methyl groups in a substance such as pentamethyl pyrrole do not yet appear to have been made, but the stereochemical studies of Bock and Adams (*J.A.C.S.*, 1931, 53, 374, 3519) on N-phenyl pyrroles, and of Chang and Adams (*ibid.*, 1931, 53, 2353) on N:N'-dipyrrolys, strongly suggest that in N-substituted pyrroles the three nitrogen valencies are co-planar. The lack of “donor” properties of the nitrogen atom and the aromatic character of the pyrrole ring also strongly support this planar arrangement. Thus, the nitrogen atoms in (IX), (X) and (XIII) all lack donor properties. In this connection it is important to recall that Manjunath claimed to have reduced (IX) electrolytically to a markedly basic substance $C_{18}H_{23}N$, which would, presumably, be formulated as (XIV). Gurney, Perkin and Plant's (*loc. cit.*) observation that the reduction of tetrahydrocarbazole leads almost entirely to cis-hexahydrocarbazole, strongly suggests that both cyclohexane rings in (XIV) would be attached in the cis positions, although, even so, there are two stereochemical possibilities for (XIV).

A substance with the structure (XIV) still conforms to the requirements of Jackson and Kenner's structure (I). It is interesting, therefore, that Manjunath's compound formed a crystalline methiodide—corresponding to (XV). A substance of this type must have a non-planar distribution of its nitrogen valencies, and here it would be most probable that one or both of the reduced pyrrole rings would be "buckled" or "puckered". We have not yet studied the reduction of (XIII), but hope to report the results of such an investigation shortly.



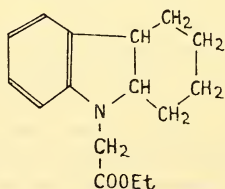
XIV.



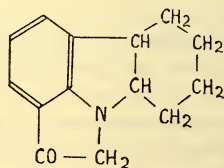
XV.

Although it has been found possible to prepare the substance (XIII), which conforms to Jackson and Kenner's requirements, we have been unsuccessful in many other attempts to prepare compounds containing the structure (I). Thus, reduction of 1-nitrosoindoline (XII) with zinc dust and acetic acid in presence of either (a) pyruvic acid, or (b) ethyl pyruvate, did not apparently lead to formation of indole derivatives, only small amounts of unchanged nitroso-indoline being recovered.

Condensation of ethyl bromoacetate with *cis*-hexahydrocarbazole led readily to formation of hexahydrocarbazole-9-acetic ester (XVI). Attempts to hydrolyse this ester to the corresponding acid, in order to attempt the cyclisation of this to (XVII) (either directly, by elimination of water, by alkaline fusion or through the acid chloride),



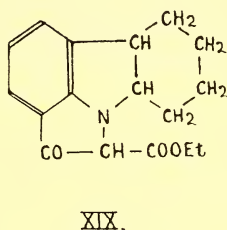
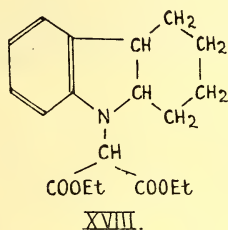
XVI.



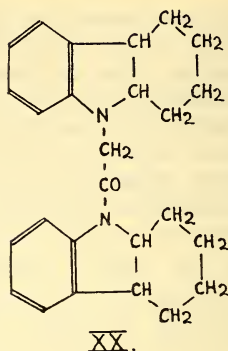
XVII.

usually resulted in the formation of much N-methyl hexahydrocarbazole (*cf.* Perkin and Plant, *J.C.S.*, 1924, 1512) owing to the great ease of decarboxylation of the acid, which was not isolated in a pure condition. Attempts to cyclise (XVI) directly by treatment with concentrated sulphuric acid under varying conditions, or by heating, all failed. It will be recalled that Perkin and Reilly (*J.C.S.*, 1923, 2399) noted the absence of any tendency of tetrahydrocarbazole-9-acetic acid to undergo ring closure.

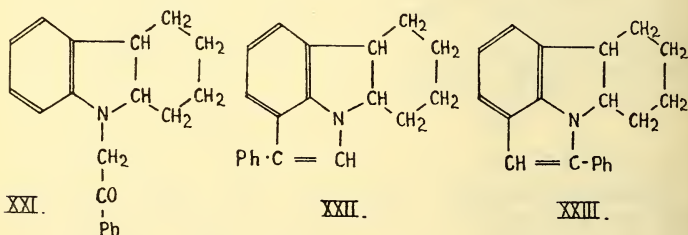
Blank (*Ber.*, 1898, 31, 1812; *D.R.P.*, 109, 416) has shown that arylaminomalonic esters can be converted by the action of heat into indoxyl esters. Hexahydrocarbazole was found to be readily converted into hexahydrocarbazole-9-malonic ester (XVIII), but it was not possible to obtain the substance (XIX) from this by heating to 280°. Careful hydrolysis of (XVIII) gave the corresponding malonic acid, which, like the acid corresponding to (XVI), very readily lost carbon dioxide and formed N-methyl hexahydrocarbazole.



Hinsberg (*Berichte*, 1888, 21, 110; 1892, 25, 2545) developed a method for the preparation of arylglycines and the corresponding aryl glycine arylamides, which could be cyclised to indoxyls. The method involves the interaction in hot aqueous-alcoholic solution of arylamines and glyoxal-bisulphite. With secondary amines of the benzene series ring-closure occurs and oxindole sulphurous esters are formed (*cf.* Hinsberg and Rosenzweig, *Berichte*, 1894, 27, 3253); and these are readily hydrolysed to oxindoles with hydrochloric acid at 80-90°. Application of this reaction to *cis*-hexahydrocarbazole led, after prolonged boiling, to a very small yield of the amide (XX). Owing to the low yield, no attempts to cyclise this product were made.

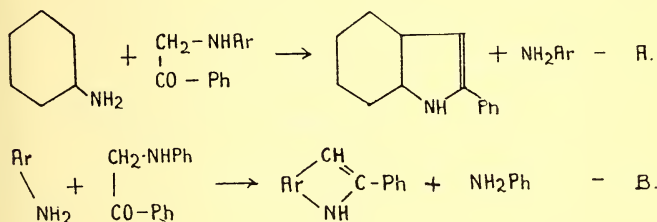


Cis-hexahydrocarbazole reacted readily with w-bromoacetophenone to give 9-phenacyl hexahydrocarbazole (XXI), but cyclisation of this substance to (XXII) or (XXIII) could not be effected with concentrated sulphuric acid, anhydrous zinc chloride, phosphorus pentoxide, or by simple heating. Möhlau (*Berichte*, 1881, 14, 173; 1882, 15, 2480; 1888, 21, 510) showed that treating phenacylaniline with concentrated sulphuric acid, or simple distillation led to formation of α -phenylindole (not the expected β -phenylindole). Later, Bischler (*Berichte*, 1892,

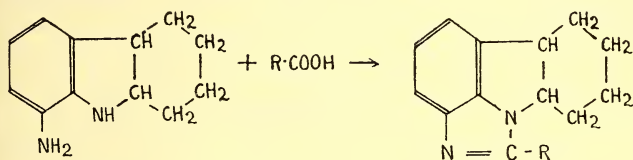


25, 2860) showed that phenacylarylamines when heated with aniline all gave the same α -phenylindole, while phenacyl aniline heated with substituted anilines gave α -phenylindoles substituted in the nucleus. When reaction B was applied to a mixture of phenacylaniline and cis-hexahydrocarbazole (heating together at 180-190° for 90 minutes) it was found that α -phenylindole was formed together with unchanged cis-hexahydrocarbazole, which acted, apparently, only as a solvent in the reaction; for heating of phenacylaniline alone at 180° for twenty minutes led to formation of α -phenylindole. It is worthy of

comment that the picrate prepared from this substance was found to crystallise in fine red brown needles melting at 139° , whereas it has been described by Möhlau (*loc. cit.*), and other authors as forming red prisms melting at 127° . It is conceivable that we have obtained another crystalline form of this picrate.



The ease with which 8-aminotetrahydroquinoline reacts with carboxylic acids to form 1:7-trimethylene benzimidazoles (*cf.* Hazlewood, Hughes and Lions, *THIS JOURNAL*, 1937, 71, 462-474) suggested that it might be possible to form substituted 1:7-ethylene benzimidazoles from 8-aminohexahydrocarbazole (or 7-amino-indoline) and carboxylic acids, according to the scheme:

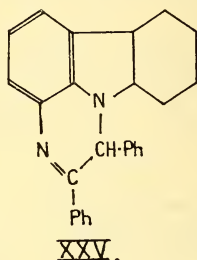


XXIV.

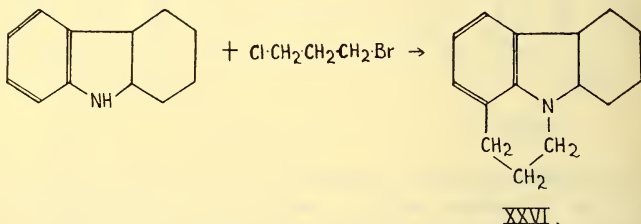
8-Aminohexahydrocarbazole (XXIV) was readily prepared by reduction with tin and aqueous-alcoholic hydrochloric acid of 8-nitrotetrahydrocarbazole (Perkin and Reilly, *J.C.S.*, 1923, 2406). However, it was found to yield only a mono formyl derivative when refluxed with absolute formic acid; although acetic anhydride converted it into a diacetyl derivative. When treated with glycollic acid in boiling 4N hydrochloric acid solution (*cf.* Phillips, *J.C.S.*, 1928, 2393) it failed to react, and could be recovered unchanged from the reaction mixture.

Treatment of (XXIV) with sodium nitrite in acetic acid solution led only to formation of tarry material, and it was not possible to isolate any crystalline triazole derivative.

On the other hand, the base (XXIV) condensed readily with benzoin in boiling glacial acetic acid solution to form the substance (XXV)—in which a nitrogen atom is a common member of 5- and 6-membered rings which are simultaneously fused to a benzene ring. Jackson and

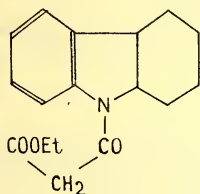


Kenner (*loc. cit.*) have pointed out that substances of this type are not uncommon, and we have been able to show that hexahydrocarbazole reacts with trimethylene chlorobromide when heated with it for 18 hours to form 8-9-trimethylene hexahydrocarbazole (XXVI). (Cf. v. Braun, Heider and Wyczatkowska, *Berichte*, 1918, 51, 1219). This base was an oil boiling at 149-151°/2 mm., readily characterised by its crystalline picrate, styphnate and methiodide.

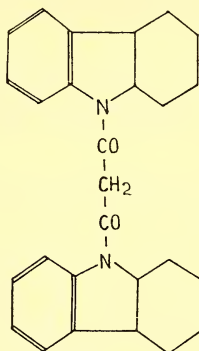


Application of the reaction discovered by Bamberger and Sternitzki (*Berichte*, 1893, 26, 1297) for the preparation of ketolilolidine derivatives from dihydroindoles and malonic ester to hexahydrocarbazole led to ready formation of the half-amide (XXVII), or the diamide (XXVIII) according to the conditions employed; but attempts to effect the cyclisation of (XXVII) led to elimination of ethyl acetate, and formation of a gummy material from which hexahydrocarbazole could be isolated together with an acid (A) and a neutral substance (B), both of which appeared to have the

molecular formula $C_{13}H_{15}ON$. They were not further investigated.



XXVII.



XXVIII.

We have also to report the results of some experiments which were undertaken as a result of the observation that 8-methyl-tetrahydrocarbazole was obtained from the distillation of the product recovered from the reduction of 9-nitroso-8-methyl hexahydrocarbazole with zinc dust and acetic acid in presence of cyclohexanone (*vide supra*). That this product resulted from the pyrolysis of unchanged 9-nitroso-8-methylhexahydrocarbazole is strongly supported by the independent pyrolysis of some nitrosohexahydrocarbazole derivatives. Thus, from the pyrolysis of N-nitrosohexahydrocarbazole it was possible to obtain hexahydrocarbazole and tetrahydrocarbazole. The 9-nitroso-6-methyl-hexahydrocarbazole described by Manjunath, on pyrolysis, gave 6-methylhexahydrocarbazole and 6-methyl tetrahydrocarbazole; and 9-nitroso-8-methyl hexahydrocarbazole on pyrolysis gave a mixture of 8-methyl hexahydrocarbazole and 8-methyl tetrahydrocarbazole. It will be recalled that Wieland and Lecher (*Annalen*, 1912, 392, 168) pyrolysed N-nitrosocarbazole in hot xylene and obtained a mixture of much carbazole and a little 3-nitrosocarbazole; and that Warquezrol and Florentin (*Bull. Soc. Chim.*, 1912, 11, 804) obtained nitric oxide quantitatively, together with some diphenylamine by pyrolysis of N-nitroso diphenylamine.

Finally, the nitration of 6-methyl-9-acetyl hexahydrocarbazole under varying conditions has been studied, and the results obtained are recorded in the experimental section. They had as their object the preparation of a

derivative of 8-amino hexahydrocarbazole, but were abandoned when 8-amino hexahydrocarbazole itself was found to be readily accessible.

EXPERIMENTAL.

In the following experiments *cis*-hexahydrocarbazole (Gurney, Perkin and Plant, *J.C.S.*, 1927, 2676) was used.

9-Carboethoxyhexahydrocarbazole.

Hexahydrocarbazole (10.4 g. ; 2 mols.) and chloroformic ester (3.3 g. ; 1 mol.) were heated together at 100° for 5 hours in absence of moisture. The reaction product was then treated with cold dilute hydrochloric acid (to remove excess hexahydrocarbazole), taken up, washed and dried in ether, and, after removal of the solvent, distilled *in vacuo*. A colourless oil boiling at 200-202°/20 mm. (yield 80%) was obtained.

Found : C=73.4%, H=7.7% ; calculated for $C_{15}H_{19}O_2N$, C=73.4%, H=7.7%.

9-Nitrosohexahydrocarbazole (VII).

This substance was prepared by the method of Borsche, Witte and Bothe (*Annalen*, 1908, 359, 49), who described it as an uncrystallisable oil. Manjunath (*loc. cit.*) claims to have obtained it as "large brown prisms from alcohol, m.p. 61-62°". The authors failed to obtain it in a solid state.

8-9-(1:2-Cyclohexylene)-Tetrahydrocarbazole (IX).

The procedure of Manjunath (*loc. cit.*) was closely followed.

A solution of nitrosohexahydrocarbazole (10 g.) in glacial acetic acid (100 c.c.) containing cyclohexanone (6.1 g.) was cooled by ice and stirred whilst zinc dust (30 g.) was added during one hour. Excess zinc dust was filtered off and the clear solution allowed to stand overnight. It was then heated on the steam bath for an hour, cooled and poured into water. The product was taken up in ether and the ethereal solution washed repeatedly with water, dilute hydrochloric acid, and dilute sodium carbonate solution. After drying, the ether was removed and the residue distilled under reduced pressure, when a colourless oil (3.5 g.) passed over at 200-210°/4 mm. Redistillation gave a fraction (2.5 g.) boiling at 190-200°/2 mm., which

soon solidified. On recrystallisation from ethanol it formed rosettes of needles melting at 77°.

Found : C=85.9%, H=8.3% ; calculated for $C_{18}H_{21}N$, C=86.3, H=8.4%.

This substance is stated by Manjunath (*loc. cit.*) to form colourless prisms melting at 83°, and boiling at 230-240°/13 mm.

o-Tolyl Hydrazine.

The following procedure was found to give improved yields of *o*-tolyl hydrazine.

The diazo solution prepared from *o*-toluidine (90 g.), concentrated hydrochloric acid (900 c.c.), sodium nitrite (61 g.), and water (200 c.c.) was added with efficient stirring to a solution of stannous chloride (550 g.) in concentrated hydrochloric acid (500 c.c.) at such a rate that the temperature of the reaction mixture did not rise above 5°. Half an hour after the addition had been completed, the thick cream-coloured precipitate was collected, washed with a little cold water, pressed well, and dissolved in hot water (4,000 c.c.). After removing tin salts by hydrogen sulphide, the solution was concentrated to a small bulk, cooled, and rendered strongly alkaline. The precipitated *o*-tolyl hydrazine was extracted with ether, the ether dried and removed. The residual oil quickly solidified to a mass of pale yellow crystals (80 g.), which after washing with a little ether melted at 54-55°, and was almost pure *o*-tolyl hydrazine.

8-Methyl-1 : 2 : 3 : 4-Tetrahydrocarbazole.

o-Tolyl hydrazine (40 g.) was dissolved in warm alcohol (80 c.c.) and treated with cyclohexanone (32 g.). After some hours long colourless rods of cyclohexanone-*o*-tolyl hydrazone filled the liquid. These melted at 59-60°. Owing to its rapid decomposition on exposure to air, the substance was not analysed.

After standing overnight, the whole mass was poured into water, extracted with ether, the ethereal solution washed with water, dried and the ether removed.

Cyclisation of the hydrazone was readily accomplished by refluxing it with glacial acetic acid (350 c.c.) for 15 minutes. After pouring into water, the dark product was taken up in ether, and the ethereal solution washed several times with dilute hydrochloric acid, dilute sodium hydroxide and water. After drying, the ether was removed, leaving

a mass of orange crystals (38 g.). Three recrystallisations from light petroleum with the aid of charcoal yielded 8-methyl tetrahydrocarbazole as colourless glistening plates melting at 98° .

Found: N=7.5%; calculated for $C_{13}H_{15}N$, N=7.6%.

The picrate separated from alcohol as dark red needles melting and decomposing at 136° .

8-Methyl-1:2:3:4:10:11-Hexahydrocarbazole.

This substance was prepared in 85% yield by the same method as that employed to prepare 6-methylhexahydrocarbazole (see below). It was a colourless oil boiling at $177^{\circ}/28$ mm.

Found: C=83.6, H=9.0%; calculated for $C_{13}H_{17}N$, C=83.4, H=9.1%.

The picrate separated from ethanol, in which it is easily soluble, as shining yellow plates which melted and decomposed at $159-160^{\circ}$.

Found: N=13.5%; calculated for $C_{19}H_{20}O_7N_4$, N=13.5%.

8-Methyl-9-nitrosohexahydrocarbazole (XI).

A solution of 8-methylhexahydrocarbazole (10 g.) in acetic acid (50 c.c. of 50%) was cooled to 0° and treated slowly with a solution of sodium nitrite (3.8 g.) in water (10 c.c.). The thick oil which separated was taken up in ether, the ethereal solution washed with dilute hydrochloric acid and water, the ether dried and removed. The residue (10 g.) crystallised after some time in the form of diamond-shaped plates. After recrystallising from light petroleum with the aid of charcoal, 8-methyl-9-nitrosohexahydrocarbazole formed large pale brown rhombs which melted at 68° . This substance is very readily soluble in the usual organic solvents.

Found: N=12.7%; calculated for $C_{13}H_{16}ON_2$, N=13.0%.

Reduction of 8-methyl-9-nitrosohexahydrocarbazole with Zinc Dust and Acetic Acid in presence of Cyclohexanone.

8-Methyl-9-nitrosohexahydrocarbazole (17 g.) dissolved in glacial acetic acid (170 g.) containing cyclohexanone (14 c.c.) was reduced with zinc dust (50 g.) and the product (0.5 g.) isolated in the same manner as in the case of nitrosohexahydrocarbazole. It boiled at $150-180^{\circ}/2$ mm.,

and was identified by its melting point and that of its picrate as 8-methyl tetrahydrocarbazole.

8 : 9-Ethylene-1 : 2 : 3 : 4-tetrahydrocarbazole (XIII).

Indoline prepared by the method of Ferber (*Ber.*, 1929, 62, 188) was converted to N-nitroso-indoline (Plancher and Ravenna, *Atti della Reale Accademia dei Lincei (Rendiconti)*, 5, 14, I, 636). A solution of nitrosoindoline (12 g.) and cyclohexanone (12 g.) in glacial acetic acid (120 g.) was treated with zinc dust (45 g.) and the product worked up as before. After removing the ether, the residual reddish brown solid (3 g.) was recrystallised three times from light petroleum with the aid of charcoal and obtained as long colourless shining needles melting at 154°.

Found : C=85.1, H=7.6%, N=7.0%; calculated for $C_{14}H_{15}N$, C=85.3, H=7.6, N=7.1%.

The picrate crystallised from ethanol as small shining yellow needles, which melted with decomposition at 141°.

Found : N=13.2%; calculated for $C_{20}H_{18}O_7N_4$, N=13.1%.

Reduction of Nitrosoindoline with Zinc Dust and Acetic Acid in the presence of (a) Pyruvic Acid or (b) Ethyl Pyruvate.

Nitrosoindoline (12 g.) dissolved in glacial acetic acid (120 g.) containing pyruvic acid (12 g.) or ethyl pyruvate (16 g.) was reduced with zinc dust (45 g.) and the reaction product isolated by the same method employed when the carbonyl compound used was cyclohexanone. In each case a small amount (0.5 g.) of unchanged nitroso-indoline was obtained, and this was the only recoverable product.

Ethyl Hexahydrocarbazole-9-acetate (XVI).

Hexahydrocarbazole (10.4 g.; 2 mols.) and ethyl bromoacetate (5.0 g.; 1 mol.) were heated together for 5 hours at 100°, and the product isolated as in the preparation of 9-carbethoxy hexahydrocarbazole. It formed a colourless viscous oil boiling at 204-206°/20 mm. (yield 80%).

Found : C=74.1, H=8.1%; calculated for $C_{16}H_{21}O_2N$, C=74.1, H=8.1%.

Many attempts to cyclise this ester were made.

(1) A solution of the ester (2 g.) in cold concentrated sulphuric acid (20 g.) was allowed to stand for 24 hours.

It was then poured on to ice and the product recovered, and found to be identical with the starting material.

(2) A similar ten per cent. solution of the ester in concentrated sulphuric acid was unaffected by heating at 100° for 1 hour.

(3) The ester (2 g.), preheated to 100° , was dropped into liquid paraffin (50 g.) at 280° and maintained at that temperature for 15 minutes. No gas was evolved, and no cyclisation occurred.

(4) The ester was heated at 300° for 15 minutes. No change other than some slight charring occurred.

Hydrolysis of Ethyl Hexahydrocarbazole-9-Acetate : formation of 9-Methyl Hexahydrocarbazole.

A solution of the ester (XVI ; 5 g.) in alcoholic potassium hydroxide solution (20 c.c. of 10%) was heated under reflux for two hours, then cooled and diluted with water, acidified with acetic acid and the precipitated oil taken up and dried in ether. After removal of the solvent the oily residue would not solidify. It was insoluble in alkalis, but dissolved readily in dilute hydrochloric acid. Eventually it was distilled *in vacuo*, a colourless oil boiling at $163^{\circ}/26$ mm. being collected.

Found : N = 7.6% ; calculated for $C_{13}H_{17}N$, N = 7.5%.

This oil readily yielded a *picrate* crystallising in lustrous orange plates from alcohol, and melting with decomposition at $146-7^{\circ}$.

Found : N = 13.3% ; calculated for $C_{19}H_{20}O_7N_4$, N = 13.5%.

The *methiodide*, obtained by heating the oil with excess methyl iodide at 100° for 15 minutes, crystallised from an alcohol-ethyl acetate mixture in colourless prisms melting at 195° .

Found : N = 4.5% ; calculated for $C_{14}H_{20}NI$, N = 4.4%.

N-methyl-hexahydrocarbazole, previously prepared by Perkin and Plant (*J.C.S.*, 1924, 1512) is described as a colourless oil boiling at $162^{\circ}/24$ mm., yielding a *picrate* melting at 143° , and a *methiodide* melting at 195° .

Diethyl Hexahydrocarbazole-9-malonate (XVIII).

Hexahydrocarbazole (20.8 g. ; 2 mols.) and diethyl bromomalonate (7.2 g. ; 1 mol.) were heated together at 100° for 5 hours. The reaction mixture was then shaken with ether and dilute hydrochloric acid, the ethereal solution separated, and the solvent removed. The

remaining oil was distilled with steam to remove unchanged bromomalonic ester. The residual oil was taken up and dried in ether and finally fractionated twice *in vacuo*, a clear pale yellow oil (yield 70% of theory) boiling at 190-193°/2 mm. being collected.

Found: C=69.1, H=7.5%; calculated for $C_{19}H_{25}O_4N$, C=69.0, H=7.6%.

No apparent cyclisation of this ester occurred when it was maintained at 280° for 15 minutes, and no crystalline substance could be obtained from the tarry reaction mixture.

Hexahydrocarbazole-9-malonic Acid.

After hydrolysis of the above described ester with alcoholic potassium hydroxide solution in the usual manner, removal of alcohol, and acidification of the diluted aqueous solution with dilute acetic acid, an oil was obtained, which was collected and dried with the help of ether. After removal of the solvent the residual oil was not completely soluble in alkali. The undissolved residue was identified as N-methyl hexahydrocarbazole. The alkaline extract was carefully acidified and the precipitated oil taken up, dried, and treated with animal charcoal in ether. The solvent was then allowed to evaporate at room temperature. The residual oil was induced to solidify by rubbing it in contact with petroleum ether. It was obtained as a pale brown powder melting at 93-95°. It redissolved almost completely in alkaline solution, but owing to the readiness with which it underwent decarboxylation could not be further purified. It was found to be very soluble in all the usual organic solvents with the exception of petroleum ether.

Found: N=5.2%; calculated for $C_{15}H_{17}O_4N$, N=5.1%.

9-Hexahydrocarbazole-9-acetyl hexahydrocarbazole (XX).

A solution of hexahydrocarbazole (6.9 g.) and glyoxal bisulphite (10.6 g.) in aqueous alcohol (300 c.c. of 50%) was heated under reflux for 30 hours. At the end of this time a small amount of solid material had separated. This was recovered and recrystallised from ethyl alcohol, being thus obtained in small colourless prisms melting at 221-222°. Further small quantities could be recovered from the

reaction mother liquor, together with much unchanged starting material.

Found: N=7.1%; calculated for $C_{26}H_{30}ON_2$, N=7.2%.

9-Phenacyl hexahydrocarbazole (XXI).

A solution of hexahydrocarbazole (20 g.) and w-bromoacetophenone (12 g.) in alcohol (100 c.c.) was heated under reflux for an hour, filtered and allowed to stand. The product soon crystallised out, and was collected and recrystallised from alcohol, being thus obtained in small yellow prisms melting at 112°.

Found: N=5.0%; calculated for $C_{20}H_{21}ON$, N=4.8%.

Attempts to Cyclise Phenacylhexahydrocarbazole.

(a) Phenacylhexahydrocarbazole (3 g.) was dissolved in cold concentrated sulphuric acid (30 g.) and allowed to stand 24 hours at room temperature. After pouring on to ice the product was recovered with the help of ether and shown to be unchanged starting material.

(b) A similar solution in concentrated sulphuric acid was heated for 1 hour at 100°. The product consisted of unchanged starting material and tarry products.

(c) Phenacylhexahydrocarbazole (4 g.) and powdered anhydrous zinc chloride (10 g.) were heated under reflux with cumene (15 c.c.) for an hour. The cumene was then removed with steam. The residual product consisted of tarry material and a little unchanged phenacylhexahydrocarbazole.

(d) A solution of phenacylhexahydrocarbazole (4 g.) in dry xylene (20 c.c.) was gently refluxed for an hour with phosphorus pentoxide (5 g.). After recovery, the product was found to be mainly unchanged starting material.

(e) Heating of phenacylhexahydrocarbazole to 180° led only to formation of tarry material.

Reaction of Phenacylaniline with Hexahydrocarbazole.

Phenacylaniline (5 g.) and hexahydrocarbazole (20 g.) were heated at 180-190° for 90 minutes. The reaction product was poured into excess dilute hydrochloric acid, well stirred, and the undissolved residue taken up and dried in ether. After removal of the solvent the residue was rapidly distilled *in vacuo* in an Anschütz flask. A

fraction boiling at 190-210°/2 mm. was collected, the higher boiling residue being tarry. The collected pale yellow fraction readily solidified. After two recrystallisations from benzene it was obtained (1.5 g.) in colourless lustrous leaflets melting at 186°.

Found: C=86.2, H=5.9, N=7.0%; calculated for C₁₄H₁₁N, C=87.0, H=5.7, N=7.2%.

The treatment of a solution of this substance in concentrated sulphuric acid with a drop of nitric acid led to rapid development of a red colour. It also gave a violet colour in the pine splinter test. Both these tests are given by α -phenylindole, which melts at 186° (*cf.* Möhlau, *loc. cit.*).

The product obtained above gave a picrate which crystallised from alcohol in fine red-brown needles melting at 139°. (Möhlau described the picrate of α -phenyl indole as melting at 127°.)

Found: N=13.3%; calculated for C₂₀H₁₄O₇N₄, N=13.3%.

Pyrolysis of Phenacylaniline—Preparation of α -Phenyl Indole.

Phenacylaniline was heated at 180° for twenty minutes, after which time water was no longer evolved. The dark product was extracted with ether, the ethereal solution washed with dilute hydrochloric acid, then with water, dried, and the ether removed. The residue on distillation yielded a fraction boiling at 200-210°/2 mm., which was identified as α -phenyl indole.

8-Amino-1 : 2 : 3 : 4 : 10 : 11-Hexahydrocarbazole (XXIV).

8-Nitrotetrahydrocarbazole (20 g.; Perkin and Riley, *J.C.S.*, 1923, 2406), alcohol (60 c.c.), concentrated hydrochloric acid (60 c.c.) and tin (60 g.) were heated together at 100° for 5 hours. After removal of as much alcohol as possible by steam distillation the liquid was decanted from undissolved tin, made strongly alkaline and extracted with ether. After drying and removal of the solvent the residual thick dark oil (10 g.) solidified rapidly on rubbing. Recrystallised from methanol and then benzene (charcoal) it was obtained in almost colourless rods melting at 159-160° (decomp.).

Found: N=14.7%; calculated for C₁₂H₁₆N₂, N=14.9%.

This diamine oxidises very readily in solutions in organic solvents. It is reasonably stable when solid. Its acid solutions are also moderately resistant to oxidation.

The *picrate* crystallises from ethanol in yellow prismatic needles melting at $172\text{--}3^\circ$ (decomp.).

Found: N=16.9%; calculated for $\text{C}_{18}\text{H}_{19}\text{O}_7\text{N}_5$, N=16.8%.

8-Formylamino-1:2:3:4:10:11-Hexahydrocarbazole.

A solution of 8-aminohexahydrocarbazole (1.5 g.) in glacial formic acid (D 1.22; 15 c.c.) was heated under reflux for 2 hours, then poured into water. The precipitated solid was collected and recrystallised from ether, and then methanol, being thus obtained in small colourless rods melting at 192° . It was insoluble in dilute acids.

Found: C=72.4, H=6.9, N=13.0%; calculated for $\text{C}_{13}\text{H}_{16}\text{ON}_2$, C=72.2, H=7.4, N=13.0%.

The product was thus a mono-formyl derivative—presumably 8-formylamino-hexahydrocarbazole. The acidic reaction mother liquors were found to contain no basic substance.

8-Acetylamino-9-acetyl-1:2:3:4:10:11-hexahydrocarbazole.

A solution of 8-aminohexahydrocarbazole (1 g.) in acetic anhydride (10 c.c.) was refluxed for 2 hours, then poured into water. The precipitated oil quickly solidified. Recrystallised from methanol it formed colourless prisms melting at 201° .

Found: N=10.0%; calculated for $\text{C}_{16}\text{H}_{20}\text{O}_2\text{N}_2$ (diacetyl derivative), N=10.3%.

This substance was insoluble in acids. No basic product was isolated from the acidic reaction mother liquors.

Condensation of 8-Amino-1:2:3:4:10:11-hexahydrocarbazole with Benzoin.

Fusion of 8-aminohexahydrocarbazole with benzoin, even under the mildest conditions, leads to formation of tarry material. However, by refluxing the base (1.3 g.) with benzoin (1.5 g.) in glacial acetic acid (10 c.c.) for 30 minutes, pouring into water, and fractionally crystallising the product from alcohol, it was possible to isolate a small quantity of yellow needles melting at 159° .

Found: N=7.8%; calculated for $C_{26}H_{24}N_2$, N=7.7%.
The substance is thus the expected condensation product (XXV).

8: *9-Trimethylene Hexahydrocarbazole (XXVI)*.

Hexahydrocarbazole (7 g.) and trimethylene chlorobromide (50 g.) were refluxed gently for eighteen hours. The reaction mixture was treated with a little dilute hydrochloric acid and then steam distilled to remove excess trimethylene chlorobromide. After basifying the residue, it was extracted with ether, the ethereal solution dried and the ether removed. The residual oil, after two fractionations under reduced pressure, yielded a colourless oil (5 g.) boiling at $149-151^\circ/2$ mm.

Found: C=84.1, H=8.6%; calculated for $C_{15}H_{19}N$, C=84.5, H=8.8%.

The *picrate* crystallised from alcohol as small yellow prisms, melting and decomposing at 144° .

Found: N=12.5%; calculated for $C_{21}H_{22}N_4O_7$, N=12.7%.

The *stypnate* formed clusters of yellow prisms from benzene, which melted with decomposition at 160° .

Found: N=12.1%; calculated for $C_{21}H_{22}N_4O_8$, N=12.2%.

The *methiodide* was obtained by heating the base with excess methyl iodide in a sealed tube, for half an hour, on the water bath. It is easily soluble in alcohol and water, and was recrystallised from alcohol-ether, being obtained as pale yellow prisms, melting at 156° .

Found: N=4.2%; calculated for $C_{16}H_{22}NI$, N=4.0%.

9: *Carbethoxyacetyl-hexahydrocarbazole (XXVII)*.

A solution of hexahydrocarbazole (10 g.) in diethyl malonate (50 g.) was gently refluxed for 9 hours. Unchanged starting material was then removed by steam distillation and the residue collected and dried in ether. After removal of the ether the thick dark oil (9 g.) was induced to crystallise, and after several recrystallisations from petroleum ether it was obtained in long colourless needles melting at 78° .

Found: N=4.9%; calculated for $C_{17}H_{21}O_3N$, N=4.9%.

This ester was soluble in all the usual organic solvents, and also in dilute sodium hydroxide solution. Its alcoholic

solution did not develop any colour with ferric chloride solution. When it was heated rapidly to 270° and maintained at that temperature for 10 minutes, effervescence occurred, and the odour of ethyl acetate was discernible in the evolved gases. After cooling, the residual viscous oil was taken up in ether and this solution extracted with dilute hydrochloric acid. Basification of this acid extract led to separation of a small quantity of hexahydrocarbazole, which was readily identified.

Treatment of the ethereal extract with dilute sodium hydroxide solution caused a brown gum to separate, which was digested with ether and hydrochloric acid solution. From the ethereal extract a yellow oil (A) could be isolated, which soon solidified. After recrystallisation from alcohol, and then benzene-petroleum ether it was obtained in rosettes of fine colourless needles melting at 168° .

Found: C=78.3, H=7.2, N=6.9%.

From the original ether extract, after treatment with acid and alkali as above described, it was possible to isolate a neutral substance (B) in small colourless needles melting at 186° .

Found: C=79.1, H=7.5, N=7.1%.

The analytical figures for both A and B approximate to those required for a compound $C_{13}H_{15}ON$, but it is difficult to suggest acceptable structural formulæ for them.

Malonyl bis-Hexahydrocarbazole (XXVIII).

Hexahydrocarbazole (5.2 g.) and diethyl malonate (2.4 g.) were heated together at 200° for some time, and the mixture worked up as described for the preceding compound. The product crystallised from methyl alcohol in colourless leaflets melting at 185° .

Found: C=77.7, H=6.9, N=6.5%; calculated for $C_{27}H_{30}O_2N_2$, C=78.2, H=7.2, N=6.7%.

6-Methyl-1:2:3:4-Tetrahydrocarbazole.

This substance was first obtained by Borsche, Witte and Bothe (*loc. cit.*), who prepared it by cyclising the p-tolyl hydrazone of cyclohexanone with dilute sulphuric acid at 100° , and reported its melting point to be 142° . Manjunath (*loc. cit.*) repeated the preparation and gave the melting point as 148° . The following method was found to give better yields (80%).

Cyclohexanone-p-tolyl-hydrazone was refluxed with five times its weight of glacial acetic acid for 15 minutes, the

solution cooled and poured into water. The precipitate was collected, washed well with water and recrystallised from alcohol, when colourless shining plates melting at 144° were obtained.

The picrate crystallised from alcohol as fine dark red needles melting at 147° .

Found: N=13.4%; calculated for $C_{19}H_{18}N_4O_7$, N=13.5%.

6-Methyl-1:2:3:4:10:11-Hexahydrocarbazole.

This substance was prepared by Manjunath (*loc. cit.*) by the electrolytic reduction of 6-methyl tetrahydrocarbazole, who reported its melting point as $43-44^{\circ}$ and its boiling point as $230-240^{\circ}/14$ mm. Its picrate is stated to melt at 174° . These values differ considerably from those recorded below.

6-Methyl tetrahydrocarbazole (6 g.), alcohol (12 c.c.), concentrated hydrochloric acid (12 c.c.) and tin (12 g.) were heated on the steam bath for 5 hours. After distilling off as much alcohol as possible, the liquid was decanted from undissolved tin, made strongly alkaline and extracted with ether. After drying and distilling off the ether, the residue was distilled under reduced pressure, when a clear colourless oil boiling sharply at $179^{\circ}/26$ mm. passed over. It failed to solidify on long standing or on rubbing with various solvents.

Found: C=83.4, H=9.2%; calculated for $C_{13}H_{17}N$, C=83.5, H=9.1%.

The picrate separated from alcohol as yellow prismatic needles melting and decomposing at 165° .

Found: N=13.6%; calculated for $C_{19}H_{20}N_4O_7$, N=13.5%.

6-Methyl-9-acetylhexahydrocarbazole.

Acetylation of 6-methylhexahydrocarbazole was readily accomplished by heating it with excess acetic anhydride on the steam bath for one hour. It crystallised from methanol as colourless needles melting at 95° .

Found: N=6.1%; calculated for $C_{15}H_{19}NO$, N=6.1%.

Nitration of 6-Methyl-9-acetylhexahydrocarbazole.

Gurney and Plant (*J.C.S.*, 1927, 1314) have shown that the products obtainable by nitration of 9-acetylhexahydrocarbazole vary according to the nitration mixture employed.

Thus sulphuric acid and potassium nitrate yield only 6-nitro-9-acetylhexahydrocarbazole, whereas with nitric acid in glacial acetic acid, 5-nitro-9-acetyl hexahydrocarbazole and 9-acetyl-10 : 11-dihydroxyhexahydrocarbazole are obtained in addition.

Careful addition of potassium nitrate (5.4 g.) over 30 minutes to a well-stirred, ice-cold solution of 6-methyl-9-acetyl-hexahydrocarbazole (12.3 g.) in concentrated sulphuric acid (90 c.c.), followed by a further 15 minutes stirring, and then pouring on to ice led to precipitation of a yellow solid. After recrystallisation from ethyl alcohol this was obtained in very pale yellow needles (8 g.) melting at 159°.

Found : N=10.3% ; calculated for $C_{15}H_{18}O_3N_2$, N=10.3%.

This substance is thus a mono-nitro derivative, and is, most probably, *6-methyl-8-nitro-9-acetyl-hexahydrocarbazole*.

Addition of 6-methyl-9-acetyl-hexahydrocarbazole (10 g.) during 30 minutes to vigorously stirred fuming nitric acid (D 1.5 ; 35 c.c.) at 0.5°, followed, after 15 minutes further stirring, by pouring on to ice, led to precipitation of a red solid. This was collected and boiled with alcohol, when a yellow crystalline residue (3.5 g.) remained undissolved. Recrystallised from glacial acetic acid, this formed yellow prisms melting at 200°.

Found : N=13.1% ; calculated for $C_{15}H_{15}O_5N_3$, N=13.2%.

The substance thus appears to be a dinitro derivative, and is, possibly, *6-methyl-5 : 8-dinitro-9-acetyl hexahydrocarbazole*. Apart from small additional amounts of this substance, no other crystalline material could be obtained from the alcoholic extract of the above product.

6-Methyl-8-Nitro-hexahydrocarbazole.

6-Methyl-8-nitro-9-acetyl-hexahydrocarbazole (2 g.) and concentrated hydrochloric acid (50 c.c.) were heated together at 100° for 2 hours. A colourless, crystalline hydrochloride separated on cooling, but the whole mixture was basified with ammonia and extracted with ether. After drying and removal of the solvent the residue was distilled *in vacuo*, when a clear orange-red oil (1.5 g.) boiling at 210-212°/2 mm. was collected. It could not be induced to crystallise.

Found : C=66.9, H=7.1% ; calculated for $C_{13}H_{16}O_2N_2$, C=67.2, H=7.0%.

The *picrate* crystallised from alcohol in very fine pale-yellow needles melting with decomposition at 160-161°.

Found: N=15.1%; calculated for $C_{19}H_{19}O_9N_5$, N=15.2%.

Pyrolysis of 9-Nitrosohexahydrocarbazoles.

The method adopted was as follows. The nitroso compound (10 g.) was placed in a Claisen distilling flask, which was then evacuated by a water pump to an initial pressure of about 30 mm. Heat was then applied. The pressure usually rose to 350-400 mm., and then dropped again to the initial pressure, when the products were distilled over, taken up in ether and the ethereal solution shaken out with dilute hydrochloric acid. Neutral materials (tetrahydrocarbazole derivatives) could then be recovered from the ethereal solution, and basic materials (hexahydrocarbazoles) by basification of the acid extract. The substances obtained were identified by their melting points and those of their picrates.

Nitroso Compound Pyrolysed.	Products Obtained.
9 - Nitroso hexahydrocarbazole (10 g.).	{ Hexahydrocarbazole (2.2 g.). { Tetrahydrocarbazole (1.7 g.).
8 - Methyl - 9 - nitroso - hexahydrocarbazole (10 g.).	{ 8-Methyl-hexahydrocarbazole (0.5 g.). { 8-Methyl-tetrahydrocarbazole (3.0 g.).
6 - Methyl - 9 - nitroso-hexahydrocarbazole (10 g.) (Manjunath, <i>loc. cit.</i>).	{ 6-Methyl-hexahydrocarbazole (1.7 g.). { 6-Methyl-tetrahydrocarbazole (2.4 g.).

ACKNOWLEDGMENT.

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N—August 2, 1939.

THE MESOZOIC STRATIGRAPHY OF THE GULGONG-COOLAH DISTRICT.

By J. A. DULHUNTY, B.Sc.
(With Plate VI and one text-figure.)

(Manuscript received, July 14, 1939. Read, August 2, 1939.)

NOTES ON ADJOINING AREAS.

The area described in this paper forms a link connecting the Mesozoic stratigraphy of the Dunedoo-Binnaway and Dubbo-Cobborah areas lying to the west, with the Goulburn River district and Merriwa-Murrurundi area to the east. The Dunedoo-Binnaway area has been mapped and described by E. J. Kenny,⁽¹⁾ and the Dubbo-Cobborah area by A. C. Lloyd⁽²⁾ in connection with the work of the Geological Survey of New South Wales on the south-eastern intake beds of the Great Artesian Basin.

The geological sequence as determined by Kenny and Lloyd, and their correlation of the two areas⁽⁶⁾ are shown in the following table.

System.	Dubbo-Cobborah Area. ⁽²⁾	Dunedoo-Binnaway Area. ⁽¹⁾
Jurassic	Erskine Beds.	Mumbedah Beds.
	Ballimore Coal Measures.	Upper Merrygoen Beds.
Lower Mesozoic ..	Lower Ballimore Beds.	Lower Merrygoen Beds.

Uniform names have been adopted for the principal subdivisions of the Mesozoic in the Dubbo-Merriwa-Gunnedah region.⁽³⁾ In terms of this nomenclature the Erskine and Mumbedah Beds come under the heading of

the Pilliga Beds, and the Ballimore Coal Measures and Upper Merrygoen Beds are equivalent to the Gowen Beds. The Garrawilla Series has not been observed in the Dubbo-Cobborah area, and occurs on the northern side only of the Dunedoo-Binnaway area. As will be pointed out later in this paper, recent work has made it possible to subdivide the Lower Mesozoic, as shown in the above table, into Triassic and Jurassic, and the basal portion of the Lower Ballimore and Lower Merrygoen Beds is now considered to be of Triassic age, while the upper Jurassic portion is equivalent to the Pottinger Beds.

In the Goulburn River district and Merriwa-Murrurundi area, which have been mapped and described by the writer,^{(3) (4)} it was found possible to make a definite distinction between Triassic and Jurassic strata. Kamilaroi beds are followed in vertical sequence by Triassic conglomerates and sandstones, which are overlain by Jurassic shales of the Comiala Series, and these are followed by beds of Jurassic sandstone known as the Munmurra Beds. It has been shown by correlation with Kenny's work in the Gunnedah-Coonabarabran district,⁽⁷⁾ that the Comiala Series includes both Gowen and Pottinger Beds, and that the Munmurra Beds are equivalent to the Pilliga Beds.⁽³⁾

THE GULGONG-COOLAH DISTRICT.

The Gulgong-Coolah area adjoins the Goulburn River district along the Main Divide to the north-east, the Dunedoo-Binnaway area to the north-west and the Dubbo-Cobborah area to the west. On the north it is bounded by the Tertiary basalts of the Liverpool Range, and to the south it extends to the vicinity of Gulgong.

In general the area consists of an old Palæozoic basement carrying outliers of Kamilaroi and Mesozoic sediments. The basement rocks constitute highly folded and metamorphosed sediments of older Palæozoic age, as well as a large area of granite which outcrops between Gulgong and the Talbragar River, along the eastern side of the area. On the western, northern and north-eastern sides there occur fringing masses of Mesozoic beds, which are continuous with the strata of the Great Artesian Basin lying to the north-west.

The Kamilaroi and Triassic rocks occurring on the eastern side of the area in the vicinity of Ulan are continuous with the beds forming the north-western margin of the Kamilaroi Basin which lies to the south-east. The old

Palæozoic rocks exposed in the central and southern portions of the area extend away to the south and south-west, where they are continuous with the large areas of Palæozoic rocks occupying central and western New South Wales.

Conditions of shoreline deposition are evident throughout the Kamilaroi and Mesozoic sediments, giving rise to much variation in the thickness and directions of sedimentation dips of the beds, and overlapping among the various strata is particularly common.

The Kamilaroi beds, which are well characterised by Upper Coal Measure fossils, occur in the form of isolated outcrops along the margin of the Triassic beds which overlap them at numerous points, so that it is common to find the Triassic lying directly on the old Palæozoic basement over fairly large areas (see Plate VI). The Triassic beds outcrop fairly extensively on the south-western side of the area, where they dip to the west, and on the north-eastern side dipping to the north-east, but the dips in each case carry the beds below the overlying Jurassic strata. The Triassic outcropping between Ulan and Uarbry is continuous with that of the Goulburn River district, where it has been subdivided into a coarse-grained lower portion and a fine-grained upper portion.⁽³⁾ These two portions have been recognised in the Triassic outcropping along the eastern side of the upper Talbragar Valley, although the upper fine-grained portion is much thinner than in the Goulburn River district. Between Uarbry and Leadville and on the south-western side of the area, the Triassic consists mainly of the coarse-grained lower portion, with small irregular developments of fine-grained sandstone, which is evidently equivalent to the upper portion.

Between Coolah and Leadville the Triassic beds outcropping on each side of the Coolaburragundy Valley are continuous to the north-west with the sandstone and conglomerates in the basal portion of the Lower Merrygoen Beds of the Dunedoo-Binnaway district. Those outcropping on the south-western side of the area increase in thickness as they pass to the west into the Dubbo-Cobborah area, where they form the basal portion of the Lower Ballimore Beds.

The line of subdivision between Triassic and Jurassic strata, as determined by fossil evidence in the Merriwa-Murrurundi area, is at the base of the Lower Comiala Series or Pottinger Beds. This horizon can be followed, by means

of clay shales and hæmatitic ironstone bands or "red beds" which the Pottinger Beds contain, into the Gulgong-Coolah area at a point near the Talbragar fossil "Fish-Beds",⁽⁵⁾ and thence across the north-eastern section of the area to the western side of the Coolaburragundy River. The horizon is clearly marked in the Mesozoic beds on the south-western side of the area, giving a sharp distinction between Triassic and Jurassic strata. In the Dubbo-Cobborah area the horizon subdivides the Lower Ballimore Beds into basal Triassic and an upper portion equivalent to the Pottinger Beds. In the Dunedoo-Binnaway area it subdivides the Lower Merrygoen Beds in a similar manner. The possibility of the lower portions of the Lower Ballimore and Lower Merrygoen Beds being Triassic was first mentioned by Kenny and Lloyd.

The shoreline conditions of deposition have had a marked effect upon the continuity of sedimentation within the Jurassic beds of the Gulgong-Coolah area, and as a result it is difficult to follow certain subdivisions which are well marked in the areas lying to the north. The occurrence of a coarse porous sandstone equivalent to the Pilliga Beds is fairly well marked. It occupies the topmost position among the Jurassic beds, occurring as outliers and fringing masses along the sides of the area, where it is continuous with the sandstone of the Munmurra Beds of the Goulburn River district to the east, the Mumbedah Beds of the Dunedoo-Binnaway area to the north-west, and the Erskine Beds of the Dubbo-Cobborah area to the west, all of which are equivalent to the Pilliga Beds.

The Jurassic strata lying between the Pilliga Beds and the Triassic vary in thickness from about 200 feet to 30 feet and in places cut out altogether where they are overlapped by the Pilliga Beds. It is believed that these Jurassic strata, separating the Pilliga Beds from the Triassic, contain the three main subdivisions of that section of the Jurassic, namely the Gowen Beds, Garrawilla Series, and Pottinger Beds, in the form of intermittent representative masses if not continuous units. This is indicated by the presence of at least two contemporaneous lava flows occurring in the Jurassic beds a little above the top of the Triassic sandstone. The flows occur in the Jurassic strata outcropping on the south-western side of the area. They consist of olivine-basalt, showing a considerable amount of deuteric alteration, and closely resemble the contemporaneous Jurassic basalts of the

Garrawilla Series, of which they are undoubtedly the equivalents. The two flows are situated about eight miles apart, each outcropping over a very small area, indicative of small isolated flows resulting from minor extrusions of basic lava at about the same time as the extensive outpourings which produced the Garrawilla Series. The basalt is separated from the Triassic by no more than thirty feet of Jurassic sediment, which is evidently equivalent to the Pottinger Beds. The overlying strata, occurring between the basalt and the Pilliga sandstone, are equivalent to the Gowen Beds.

A distinction cannot always be made between the Gowen and Pottinger Beds unless the Garrawilla Series is present, but it is probable that the Pottinger Beds are discontinuous along the margin of the Jurassic sediments on the south-western side of the area, being overlapped at numerous places by the Gowen Beds. At several points the Gowen Beds overlap both Pottinger Beds and Triassic sandstone, and lie directly on the old Palæozoic basement. Garrawilla basalts have not been recognised in the Jurassic on the north-eastern side of the area, but it is probable from the general nature of the sediments and their relationship to the beds of the Goulburn River district that both Gowen and Pottinger Beds are present, the latter predominating. This indicates that there is a tendency for the Gowen Beds to be overlapped by the sandstone of the Pilliga Beds, as they pass to the north-east.

A sill of dolerite occurs at Mebul, about twelve miles to the west of Gulgong. The rock is a type of quartz-dolerite, in which the quartz occurs as small irregular grains, and does not take the form of an interstitial micrographic intergrowth with felspar as in the usual quartz-dolerite. It also contains large plates of ilmenite up to two centimetres in diameter and felspar laths up to five centimetres in length. The rock has been deuterically altered and contains interstitial masses of chloritic material. The sill appears to occur as an interformational mass between Triassic and Jurassic beds at a point where the former is overlapped by the Jurassic. At one place the outcrop of the dolerite is very close to the Palæozoic rocks, and it is probable that it is in contact with them on the western side of the sill where the Triassic cuts out in the overlap (see section A-B, text-fig.).

The work already referred to which has been carried out by Kenny and Lloyd in the districts between Dubbo

LEGEND

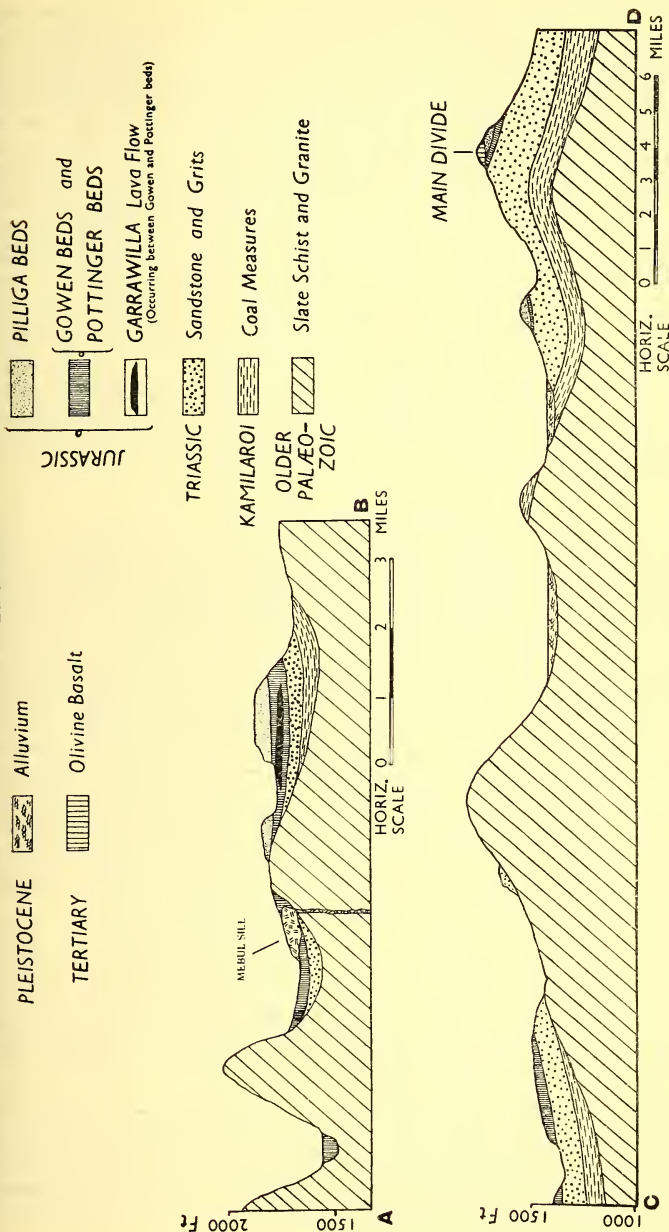


Fig. 1. Geological Sections along the lines A-B and C-D on Plate VI.

and Gunnedah, together with that described in the present paper, as well as previous work in the districts between Gulgong and Quirindi carried out by the writer to which reference has already been made, constitutes the mapping and description of the Mesozoic stratigraphy of an area of approximately 8,000 square miles. In this area the actual south-eastern boundary of the Jurassic strata associated with the intake beds of the Great Artesian Basin has been mapped from Dubbo in the south to Quirindi in the north, and the extent and distribution of the outcrops of the various subdivisions have been determined. It is now possible to summarise the Mesozoic stratigraphy of the whole area, for which purpose the accompanying table of correlation has been compiled. For the detailed stratigraphy of the various areas reference should be made to the original descriptions, as indicated by the reference numbers. The table includes certain correlations made by Kenny and Lloyd.⁽⁶⁾

STRUCTURAL NOTES.

Along the western and north-western sides of the area the general direction of dip in the Kamilaroi and Mesozoic beds is to the north-west, while on the eastern side it is to the north-east, as illustrated in section C-D, text-fig. The old Palæozoic rocks outcropping in the central portions of the area rise above the general level of the younger beds, and represent an old ridge of basement rock which extended out into the Kamilaroi and early Mesozoic lakes in the form of a partly submerged promontory. The predominating dips to the north-west and north-east on each side of this old promontory represent sedimentation dips. This is indicated by the thinning and overlapping of the strata as they approach the shorelines of deposition along the sides of the old Palæozoic landmass.

Post-Jurassic warping has affected the beds to some extent, having produced the anticlinal structure which forms the Main Divide on the eastern side of the area. Such warping may be distinguished from sedimentation dips by the fact that the beds do not thin out as they pass over the anticlinal structures.

In the vicinity of Mebul, on the south-western side of the area, the actual margins of the lakes which existed in Kamilaroi and early Mesozoic times can be traced among the masses of Palæozoic rocks which formed landmasses. An excellent example of this can be seen near the heads of

TABLE OF CORRELATION SUMMARISING THE MESOZOIC STRATIGRAPHY OF THE DUBBO-MERRIWA-GUNNEDAH REGION.

System.	Uniform Names for Major Subdivisions.	Dubbo-Cobborah District. (a)	Dunedoo-Binnaway District. (1)	Gulgong-Coolah District.	Goulburn River District. (4)	Merriwa-Murrumbidgee District. (a)	South-eastern Liverpool Plains and Coonabarabran-Gunnedah District. (7)
Jurassic.	Pilliga Beds.	Erskine Beds.	Mumbedah Beds.	Pilliga Beds.	Mummurra Beds.	Mummurra Beds (No outcrops).	Pilliga Beds.
	Gowen Beds.	Ballimore Coal Measures.	Upper Merrygoen Beds.	Gowen Beds.	Upper Comiala Series.	—	Purlawaugh Beds.
	Garrawilla Series.	—	—	Isolated Garrawilla Lava Flows.	Tuffaceous Shales. (No Basalts.)	—	Garrawilla Series.
	Pottinger Beds.	Lower Ballimore Beds, in part.	Lower Merrygoen Beds, in part.	Pottinger Beds.	Lower Comiala Series.	Lower Comiala Series.	Napperby Beds.
Triassic.	Upper Portion.	Basal Portion of Lower Ballimore Beds.	Basal Portion of Lower Merrygoen Beds.	Upper Portion (Discontinuous).	Upper Portion.	Upper Portion.	—
	Lower Portion.	—	—	Lower Portion.	Lower Portion.	Lower Portion.	Digby Beds.

Goolma and Cudgebegong Creeks, where younger sediments form the floors of valleys carved out of Palæozoic rocks, and represent deposits in bays and estuaries which existed along the old shoreline. This situation is illustrated in section A-B, text-fig. The lake in which the Pilliga sandstone was deposited seems to have been more extensive than those preceding it. Thick beds of the sandstone have no doubt covered and preserved, throughout the ages, the ancient shoreline topography which is now being exposed by erosion.

NOTES ON THE LITHOLOGY OF THE KAMILAROI AND MESOZOIC SEDIMENTS.

Kamilaroi.

An outstanding feature in the coal measure beds is the persistent occurrence of white chert bands, similar to those which characterise the Upper Coal Measure sediments of the Kamilaroi Basin. The white chert bands retain their extremely fine-grained nature right up to the actual shorelines of sedimentation. A large quantity of rather coarse-grained tuffaceous sandstone is present in the measures, and soft tuffaceous conglomerate is not uncommon. Clayshales and mudstones are rather sandy and limited in extent. Dirty coal seams and carbonaceous shales are also limited in occurrence and form small irregular beds. At the base of the Kamilaroi there frequently occur beds of sandy conglomerate which may represent Upper Marine sediments, although no fossil evidence or glacial material has been found. Glacial boulder beds, however, were found by Kenny⁽¹⁾ in the Dunedoo-Binnaway area on about the same horizon.

Triassic.

As already mentioned there is little evidence of the fine-grained upper portion of the Triassic. The beds consist of conglomeratic sandstone and in places medium-to fine-grained conglomerate, the included pebbles being mainly white quartz with a limited amount of red and black jasper, chert, and hard metamorphic rocks. At several places along the south-western side of the area, there occurs near the base of the Triassic a coarse fragmentary material which could be described as a conglomerate breccia. It contains both rounded and angular fragments of Palæozoic rocks and Kamilaroi shales and chert. This material appears to be of Triassic age,

and is made up of freshly transported older Palæozoic rock debris as well as redistributed fragments of Kamilaroi sediments.

Pottinger Beds.

These basal Jurassic beds consist largely of sandy shales, sandstone and mudstones. Hæmatitic ironstone bands, known as "red beds",^{(1) (2) (3)} are present but not plentiful, although ferruginous sandy shales are common, giving a brownish-red coloration to the beds. Near the actual shorelines the shaly sandstones frequently contain small rounded pebbles giving a slightly conglomeratic nature to the beds. Rough casts, carbonaceous remains, and ferruginous replacements of fragmentary plant material are characteristic throughout the sediments.

Garrawilla Series.

The basic lavas already referred to consist of fine- to medium-grained olivine-basalt which closely resembles the Tertiary basalts, the only difference between the two being a tendency for more deuteric alteration in the case of the Jurassic lavas. Deuteric minerals are common in the Garrawilla basalts, although they are not so abundant in the flows of the Gulgong-Coolah area as in those of the Gunnedah-Coonabarabran district.

Gowen Beds.

These sediments consist mainly of highly ferruginous shales with sandy bands, and contain numerous "red bed" horizons. The thin coal seams which occur in the Gowen Beds of the Dubbo-Cobborah district,⁽²⁾ are absent in the Gulgong-Coolah area, and the beds as a whole are somewhat more sandy as a result of the shoreline conditions of deposition. Replacements in the form of ferruginous concretionary material and casts of fragmentary plant remains are scattered throughout the beds. The highly ferruginous nature of the Gowen Beds appears to indicate the existence of climatic conditions favouring the oxidation of iron-bearing substances before and during deposition, and it is also probable that volcanic products may have played a part in the formation of the beds.

Pilliga Beds.

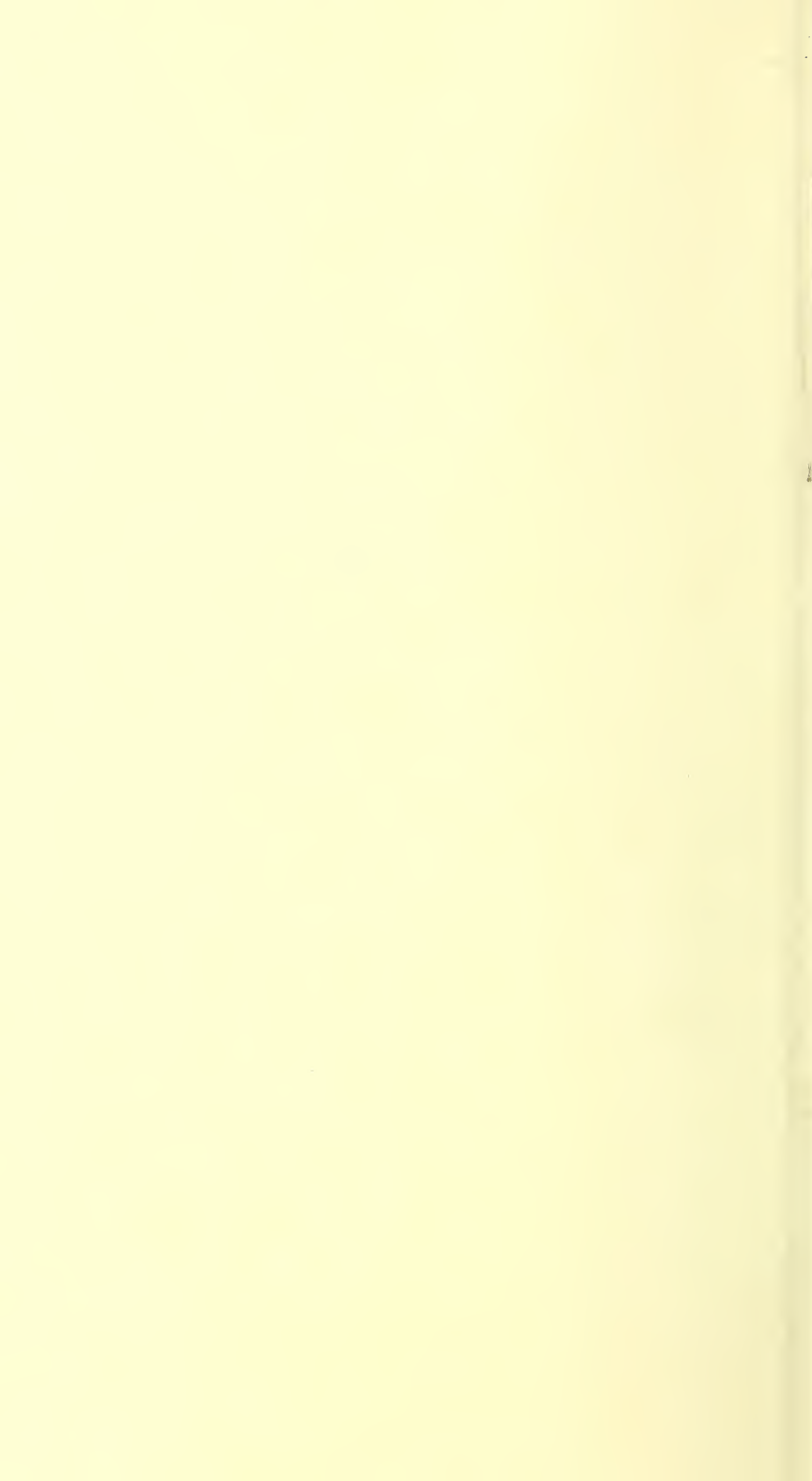
The sandstones and grits of the Pilliga Beds pass from one area to another with very little change in their lithology.

They form massive beds of coarse porous sandstone and grits, somewhat more ferruginous than the Triassic sandstones, resulting in a characteristic light-yellowish-red coloration. They are typically even-grained and although they develop a marked coarseness along the margins of deposition, they do not become conglomeratic as in the case of the Triassic sediments. They contain numerous ferruginous concretions resulting from the replacement of large fragments of wood and other plant debris. The concretions often consist of an outer shell of hard black crystalline hæmatite, partly filled with red or yellow ochre. Casts and impressions of woody material are also common. The coarse basal conglomerate which occurs in the Goulburn River district⁽⁴⁾ is not typical in the Pilliga sandstone, and does not extend into the Gulgong-Coolah area. It appears to have been developed locally near the mouth of a large Jurassic river.

The presence of the Pilliga sandstone seems to indicate a return to conditions of sedimentation somewhat similar to those which produced the massive sandstones of Triassic time, but the water-currents along the shorelines were not so strong, and the climatic influences introduced at the commencement of Jurassic sedimentation, responsible for the red coloration of the Gowen and Pottinger Beds, continued to operate during the deposition of the Pilliga sandstone.

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STUDIES IN METAMORPHISM AND ASSIMILATION IN THE WELLINGTON DISTRICT, N.S.W.

I. HYBRIDISATION IN THE WUULUMAN CREEK INTRUSION.*

By ELIZABETH M. BASNETT, B.Sc.

(With seven text-figures.)

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1. INTRODUCTION AND PREVIOUS RECORDS.

Wellington is situated on the main western railway 255 miles from Sydney, at the junction of the Bell and Macquarie Rivers. The Wuuluman Creek intrusion crops out $10\frac{1}{2}$ miles to the east of the town in the parish of Wuuluman, and is crossed by the Wuuluman road $1\frac{1}{2}$ miles

* This work was carried out at the University of Sydney during the tenure of a Commonwealth Research Scholarship, and when the writer was part-holder of the Deas-Thomson Scholarship for Geology and the John Coutts Scholarship.

east of Poggy Creek. The intrusion, which measures $1\frac{3}{4} \times \frac{1}{8}$ miles, invades folded Silurian sediments, and consists of an earlier dolerite and a later keratophyre, which has injected and hybridised the dolerite; this suggests that they were consanguineous. The north-west part of the igneous mass and the adjacent sediments have suffered shearing due to movement along a fault-plane. The Wuuluman granite, which crops out about half a mile to the north of this intrusion, does not exhibit shearing, and appears from the field evidence to be later than the fault. It is most likely, therefore, that the Wuuluman Creek intrusion is pre-granite.

No petrological work has been published on the Wuuluman Creek intrusion, but Matheson (1930) and L. J. Jones (1935) have mapped the area, and the latter has kindly allowed the present writer to examine some of the microslides belonging to the N. S. Wales Geological Survey. During 1938 Miss M. J. Colditz and the writer carried out further geological mapping, and it is hoped that the map will be used in connection with some later work.

2. NATURE OF THE INTRUSION.

The main part of the intrusion has an east-west elongation. Small outcrops of dolerite are found at distances varying from 10 to 30 chains to the south-west, north, and east. To the south the Wuuluman Hills, situated just south of the Wuuluman road, may cover other masses. These outcrops would appear to be tongues of dolerite from the main mass which have penetrated the surrounding sediments. It would seem that the intrusion is a small boss rather than a dyke as suggested by the shape of the main outcrop.

The keratophyre has a rather sporadic distribution (see map). On the eastern side of the intrusion in Por. 69, Par. Wuuluman, a fairly large mass is exposed on the top of the hill, and several smaller ones occur to the east, while in the western part of the area smaller rather dyke-like outcrops and veins invade the hybrids. Only the largest outcrops of keratophyre are shown on the map. Surrounding the keratophyre intrusion are spotted hybrids, indicating that they were produced by the injection of the keratophyre into the dolerite, while the occurrence of wide areas of spotted hybrids within the dolerite suggests that the keratophyre is not far below the present surface. Since the dolerites crop out on the hill in the western part

GEOLOGICAL SKETCH MAP
OF THE
WUULUMAN CREEK INTRUSION

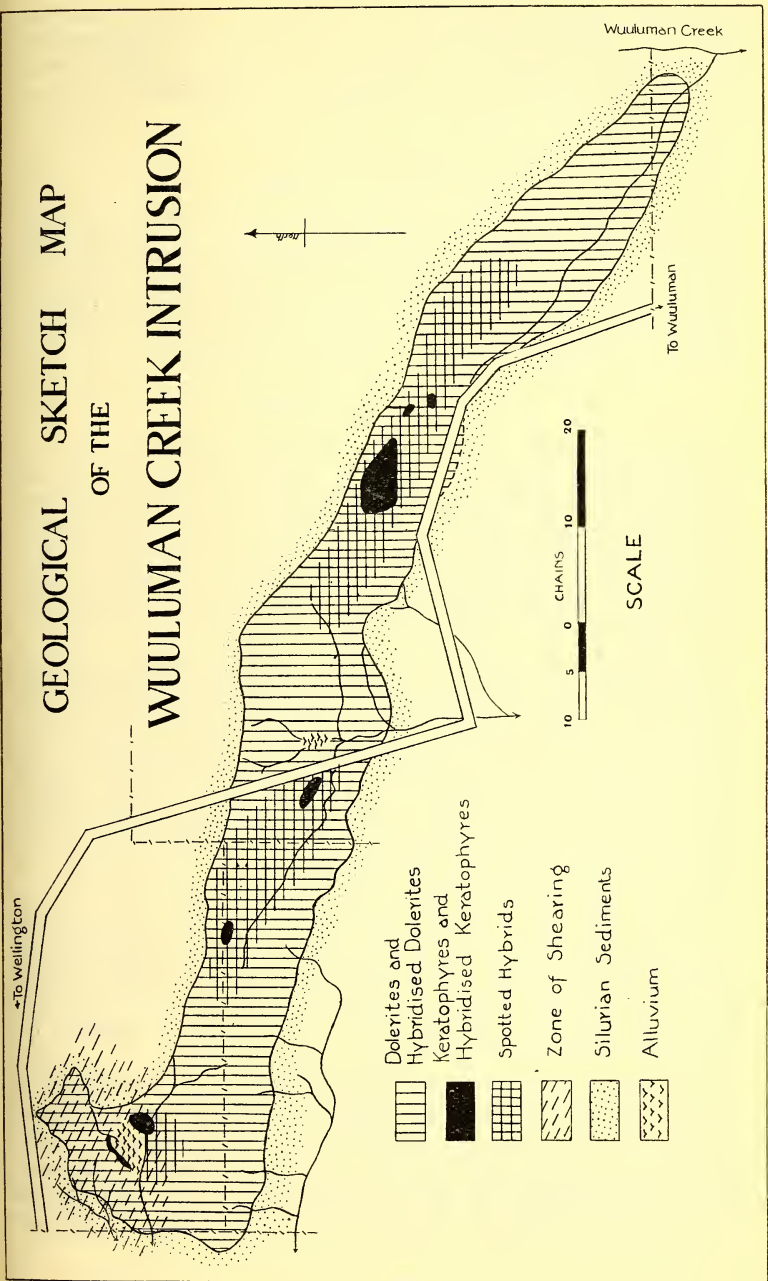


Fig. 1.

of the intrusion, and patches of spotted hybrids are found within the keratophyre to the east, it would seem that the younger intrusion was enclosed within the dolerites and did not penetrate to the surrounding sediments.

3. PETROGRAPHY.

(i) The Parent Rocks.

With regard to the nature of the original rocks little can be said with certainty, as all samples of the basic type are either hybridised or partially metamorphosed, and the acid phase has been considerably modified by the incorporation of disintegrated xenoliths, so that it is unlikely that any unaffected material will be revealed.

(a) The Altered Dolerites.

The altered dolerites show slight variation both in mineral composition and texture. The greater part of the mass has an ophitic to slightly poikilitic texture, due to the development of masses of augite and possibly of some hornblende, but in places these tend to develop their own crystal form. The ophitic fabric seems to be an original structure. Zoning and twinning were fairly common in the augite.

In the more eastern portion of the intrusion elongated masses (10 mm. \times 0.5 mm.) of fibrous uralite, or criss-cross flakes of biotite, associated with abundant iron ore, indicate the presence of long crystals of hornblende in the original rock. In this rock the felspar crystals are larger and better formed. This type, however, is not widely distributed and probably represents a slightly more acid differentiate of the doleritic magma, and could best be called a hornblende-bearing dolerite.

The plagioclase is nowhere unaltered, so that the original composition cannot be determined, but the abundance of epidote granules would indicate that it was a fairly basic type. The fairly frequent arrangement of epidote granules into zones is probably due, at least in part, to original zoning in the felspar.

Apatite is present in varying degrees as well-formed prisms up to 0.75 mm. in length, exceptionally reaching 5 mm. It is mostly pale bluish to purplish grey and contains many minute iron ore inclusions, generally arranged parallel to the elongation, but sometimes unoriented. Another peculiarity of this apatite is that it

is hollow, giving the cellular structure often shown by tourmaline, and the central portion is now largely filled with green biotite. Ilmenite in grains up to 1.5 mm. long and often showing skeleton structure is very abundant.

This rock has been called an altered dolerite for the following reasons: (i) There are indications of an original ophitic fabric. (ii) In the sheared zone there is a dynamically altered type which contains albite but no quartz (see p. 181). The absence of quartz would suggest that the rock has not been hybridised, so that the anorthite-molecule must have been removed previously. It seems probable therefore that the rock had been deuterically altered before the injection of the keratophyre magma. (iii) The analysed rock agrees fairly closely with other altered dolerites (see Table II, columns I and VI).

(b) The Keratophyres and Quartz Keratophyres.

These types are fine- to medium-grained hypidiomorphic granular rocks. All specimens have been considerably hybridised, but much of the assimilation has been mechanical, so the nature of the original rock may be surmised. The chief constituents are idiomorphic albite crystals ($Ab_{91}An_9$ to $Ab_{99}An_1$), orthoclase, quartz, and possibly some biotite. The variation in the composition of the plagioclase may in part be due to assimilation. Quartz fills interstices or is associated with albite or orthoclase in micrographic intergrowth. Dust-like inclusions, sometimes showing parallel arrangements, are fairly common in the quartz. Deuteric alteration of the albite by potash-bearing solutions fairly commonly results in the formation of micropertthite.

Little can be said regarding the original ferromagnesian minerals, as the rock contains large quantities of criss-cross flakes of biotite, grains of ilmenite, magnetite, a little pyrite, and granules of epidote, most of which have evidently been derived from the disintegration of dolerite xenoliths. However, it is probable that the pyrite and some of the magnetite belong to the keratophyre, as they are generally absent from the dolerites.

Apatite is not abundant in the main body of the mass, but it is very well developed in association with keratophyre veins found penetrating the spotted hybrids. It is usually formed along the edge of the vein or within the adjacent rock with the elongation of the crystals parallel to the length of the vein (see Fig. 6 A). The prisms are small,

colourless, and show no cellular structure and so may be easily distinguished from the apatite of the dolerite.

On account of its texture and chemical composition this rock may be called a keratophyre (see Table II, column V). Quartz was not abundant in the analysed rock, but there are others which may be called quartz-keratophyres.

(ii) Hybrid Rocks.

The hybrid rocks are formed both by the incorporation and mechanical disintegration of fragments of dolerite in the invading keratophyre magma, and by the percolation of these solutions through the rocks of the earlier intrusion. Naturally there is a region where it is difficult to decide whether the hybrid belongs to the first or to the second group, and it is here that most of the rocks which have a peculiar spotted appearance belong.

(a) Hybridised Dolerites.

In the normal dolerite, which is the most abundantly developed type, the progressive mineralogical changes produced by the introduction of solutions from the keratophyre are most clearly shown.

The augite is changed completely to uralite. It is a pale green hornblende, X=yellow green, Y=deeper yellow green, Z=blue green. $X < Y < Z$, optically negative, with positive elongation, $Z \wedge c = 31^\circ$. The original polysynthetic twinning of the augite is very well preserved, often being oblique to the elongation of the fibrous crystals. Included felspar laths are often completely replaced, and sometimes changes in the direction of growth of the fibres are produced due to the arrangement of cleavage cracks in the felspar.

The originally basic felspar is completely albitised and the anorthite molecule has apparently been removed in solution. The composition now is $Ab_{95}An_5$ to $Ab_{92}An_8$. Clouding (Macgregor, 1931) is sometimes found in the plagioclase. With slightly more impregnation rims of clear, often untwinned, albite are visible around the plagioclase of the dolerite. Very often at about this time clinozoisite and epidote are developed in the original plagioclase. The arrangement of these minerals is somewhat variable. In many cases they form tiny granules showing a greater concentration towards the edge of the laths; in others they are found throughout the mineral, giving it a greyish appearance; yet others show tiny granules around the edge, with prisms up to 0.1 mm.

in length towards the centre. These are often found in association with sericite, which has a sporadic distribution throughout the hybrids and is in places developed to the exclusion of albite in the altered felspars.

At the stage when rims of acid felspar are formed round the originally basic felspar, small needle-like crystals and fibrous masses of green hornblende crystallise from the surrounding hybrid magma. Later, with the introduction of solutions containing some potash also, this hornblende and the uralite become unstable and are replaced by masses of criss-cross flakes of biotite. It is greenish to brown in colour and develops first between the fibrous crystals, and often greenish brown patches enclosed by deep blue-green material can be seen in the surrounding uralite. This generally precedes the formation of the biotite. Around the edges of the uralitic masses, and sometimes as an outer zone to the hornblende which has crystallised from the hybrid magma, a deeper green to bright blue-green amphibole is developed. This is most likely a more actinolitic variety. With greater impregnation all the hornblende is gradually replaced by flakes of biotite, but the change is complete only in the most acid spotted hybrids.

During these changes tiny needles of hornblende, or biotite flakes, are formed in places in the felspar, and they are probably produced from small quantities of included chlorite. There is also a gradual change in the ilmenite, narrow rims develop round the larger grains, gradually replacing the mineral, and the skeleton masses are now represented by compact masses or minute crystals of brown sphene.

These alterations in the dolerite are accompanied by a gradual increase in the quantity of keratophyre solution introduced. First, rims of albitic plagioclase develop round individual felspar laths, penetrating along cleavages or surrounding groups of laths, while close by no rims are found. Generally they tend to preserve the shape of the surrounded mineral, and where interstices are left they are filled with quartz, which may be partially intergrown with the felspar. With increasing injection "pools" (Nockolds, 1938) of hybrid keratophyre magma are produced, due to the further separation of the plagioclase laths. These are roughly rounded patches of albite and quartz showing varying degrees of intergrowth and dispersed biotite flakes, surrounded by the lath-shaped plagioclase crystals of the

dolerite (Fig. 2 A). The quartz may have regular boundaries or may merge into micrographic intergrowth with plagioclase and show no signs of strain; but in other places it is strained and granulated, and material containing biotite and epidote, with or without albite, is found between the grains. Undulose extinction may be the result of strain due to shearing, but the other phenomena seem to indicate that some of the quartz which crystallised at the time when the albite rims were formed has been broken up by a later injection of the hybridised keratophyre magma. Sometimes considerable corrosion of the original basic feldspars has taken place and they are now reduced to irregular masses of epidote granules, with associated albite or sericite, surrounded by hybrid keratophyre material or flakes of biotite. The presence of microperthite in some of the "pools" and in the rims surrounding the feldspar cores indicates a partial replacement of albite by orthoclase, and suggests a sporadic concentration of potash towards the end of crystallisation. This is also shown in the keratophyre itself (see p. 165).

Towards the eastern end of the intrusive mass the injection of hybrid keratophyre magma has not been so peaceful, and disintegration of the replaced augite crystals with marked strewing of the biotite flakes, accompanied by a reduction in the grain size of the plagioclase laths, has taken place. "Pools" are still found (3 mm. across) but they contain many tiny flakes of biotite (Fig. 2 B). Here quartz is less abundant, intergrowth is not found and feldspar is in small irregular grains, or has a tendency to be lath-shaped. The apatite of the original rock has been broken along the transverse parting and tiny needles of apatite, derived from the keratophyre, also occur. The original plagioclase of the dolerite now has the composition $Ab_{96}An_4$ but albite rims are not developed. Also the keratophyre solutions, often containing flakes of biotite, have penetrated along the cleavage cracks and reduced the grain size from 3 mm. to 1 mm. or less (Joplin, 1935). Considerable bending and separation of the cleavage blocks has often resulted. The displaced anorthite molecule has not formed epidote or clinozoisite within the feldspar, but is most likely responsible for the large quantities of tiny epidote granules in the surrounding matrix.

An analysis of a hybridised dolerite is given in Table II, column II.

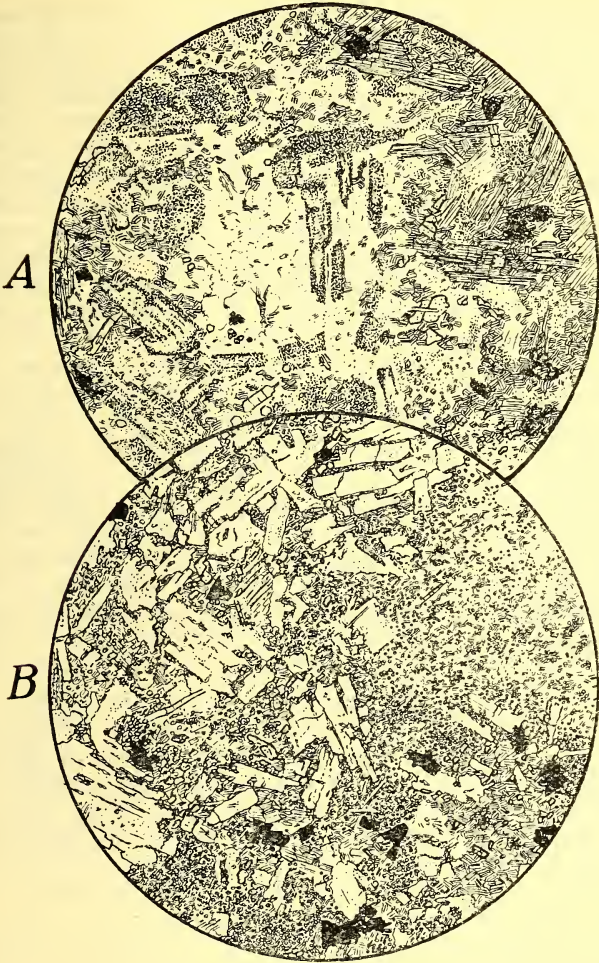


Fig. 2. Hybridised Dolerites.

- A. Considerably hybridised dolerite with keratophyre pools. The albitised basic felspar contains separated epidote and clinzoisite, sometimes showing a zonal arrangement. Occasionally sericite is associated. Uralitised augite is partially changed to biotite with some epidote and only slight scattering of flakes has taken place. Ilmenite is replaced by sphene. $\times 13$.
- B. More intensely hybridised dolerite in which less peaceful penetration has caused scattering of the biotite flakes obliterating the original ferromagnesian minerals. Remnants of one are still visible in the south-east quadrant. Reduction in grain size of the felspar is shown. Indication of a "pool" is found in the north-east quadrant. Epidote and clinzoisite are found as tiny granules and some fibrous hornblende is shown. $\times 13$.

A slightly different type is produced by the hybridisation of the hornblende-bearing dolerite (Fig. 3 A). The elongated hornblende crystals are first changed to pale green uralite, with the separation of much ilmenite. With increasing hybridisation the uralite is changed to criss-cross flakes of biotite, which is green unless associated with iron ore, when it becomes brown. Scattered grains of ilmenite have an outer rim of brown biotite, and an inner one of sphene. The original zoned plagioclase crystals have been albitised, and in the core granules of clinozoisite and epidote have developed. Later potash solutions, concentrated towards the end of crystallisation, have produced sericite in the central core and micropertthite in the outer zones. Filling the interstices, forcing the plagioclase laths apart, and causing bending of the original hornblende crystals, is material derived from the keratophyre magma. It consists of micropertthite, quartz, and albite which often form micrographic intergrowths. The albite generally shows very fine multiple twinning. Healing of cracks in the originally basic plagioclase, by intergrown quartz and plagioclase, is fairly common. In this type there is no rim of albite round the original plagioclase of the dolerite, although it has been albitised.

(b) Spotted Hybrids.

The spotted hybrids merge almost imperceptibly into the hybrid dolerites on the one hand, and into the keratophyres on the other. They differ from the hybrid dolerites in that the spots are composed chiefly of dispersed flakes of biotite, with associated minerals precipitated from the hybrid magma, and are clearly visible in the hand-specimen. With the introduction of hybrid material they show a gradual increase in size up to a certain point (about 1.5 cm.), when they rapidly decrease. At this point the rock could more correctly be termed a basified keratophyre, for the decrease is due to mechanical disintegration of many small xenoliths in a fluid magma. The spots are not rounded but irregular in shape and tend to be linked together (Fig. 3 B).

These rocks vary from types in which the position, and sometimes the shape, of the original ferromagnesian minerals is preserved by compact masses of biotite with remnants of uralite, to those in which the mineral has been obliterated through the complete replacement of the uralite by biotite and the strewing of these flakes in the

incoming hybrid magma. Epidote is ubiquitous, but much of it is precipitated at a later stage.

The disruption and separation of the originally basic plagioclase laths vary greatly even over a short distance. They are separated by a finely granular matrix (<0.25 mm.) of quartz, albite and sometimes microperthite (micrographic intergrowth is not common), and, where disruption of ferromagnesian minerals has taken place, biotite flakes, iron ore, and epidote are found. The biotite may form compact masses of tiny flakes, while the hybrid material between the plagioclase laths is fairly free from dark coloured minerals, or the spots may spread

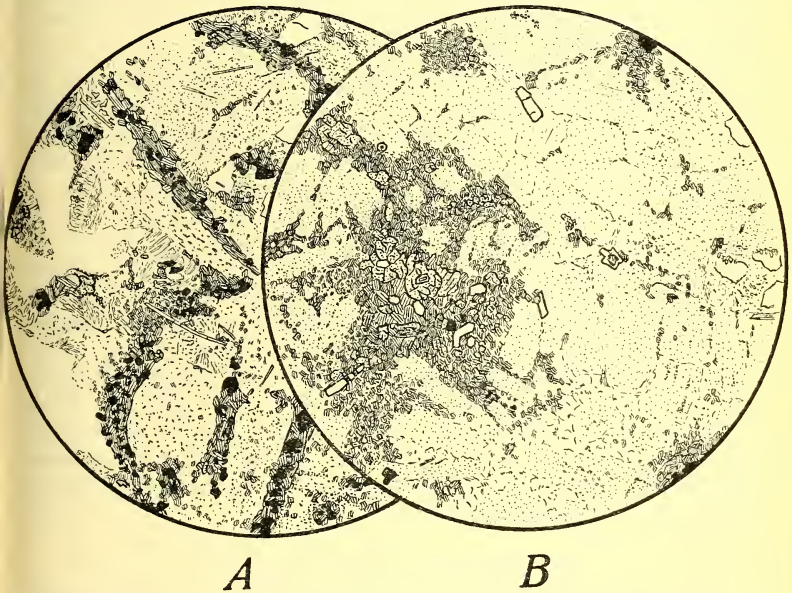


Fig. 3.

- A. Hybridised Hornblende Dolerite. The hornblende is replaced by criss-cross flakes of biotite, iron ore and a few small granules of epidote. Quartz and albite, in places showing micrographic intergrowth, have developed from the incoming keratophyre magma. $\times 13$.
- B. Biotite-rich Spotted Hybrid. In this type the original ferromagnesian minerals have been completely altered to criss-cross flakes of biotite with associated epidote. Apatite has been broken into segments. Within the spotted area the felspar has been reduced in grain size. Some scattering of biotite flakes has taken place. $\times 13$.

out for considerable distances in the hybrid rock. A reduction in grainsize of the plagioclase similar to that described for the hybridised dolerites occurs within many of the spotted areas. As in the previous types, the biotite and associated epidote and iron ore have been largely derived from the original ferromagnesian minerals of the dolerite, and the changes noted in the hybrid types are also present here, with biotite in much greater abundance. The green amphibole which crystallised from the hybrid magma in the altered dolerite is only occasionally found, and only one specimen with slightly altered uralite and hybrid hornblende has been collected. The formation of epidote granules within the originally basic felspar laths is present only in types closely related to the hybridised dolerites.

Ilmenite is altered almost entirely to compact masses of brown sphene, small grains of pyrite give place to hematite or are surrounded by it, and square crystals of magnetite remain unchanged. Grey cellular apatite derived from the dolerite is found, together with considerable quantities of clear, needle-shaped, and rod-like crystals of apatite from the hybrid magma; the latter is most noticeable in association with the spotted areas. As in the hybrid dolerites, sericite is sometimes present in the altered plagioclase to the exclusion of albite. Purplish brown tourmaline forms crystals and columnar aggregates up to 1.5 mm., which occasionally show slight radiating structure. Pleochroism is marked, O=dark brownish blue, E=light purplish brown, O>E, orientation negative. It is present in small quantities in both spotted hybrids and hybridised dolerites. Analyses of two spotted hybrids are given in Table II, columns III and IV.

(c) Hybridised Keratophyres.

The spotted hybrids pass into hybridised keratophyres where mechanical disintegration by the hybrid magma has produced complete strewing of the small dolerite xenoliths (Nockolds, 1933). The ferromagnesian minerals representing dispersed xenoliths occur in small clots consisting of biotite, epidote, magnetite, and ilmenite (almost completely changed to sphene). Attached to these clots are strings of biotite flakes, epidote, and iron-ore granules, which extend out between the laths of felspar and closely resemble structures of similar origin in the Dhoon granite (Nockolds, 1931). The biotite ranges in colour from fairly

dark brown to bluish green, over very short distances; the former is usually associated with iron ore and is probably a more ferriferous type. For the brown variety, X=straw yellow, Y=brownish grey, Z=deep greenish brown; green variety, X=straw yellow, Y=greenish grey, Z=deep green. For both types $X < Y \leq Z$.

The originally basic felspar may contain flakes of green biotite along the cleavage cracks, which is due either to chloritic material contained in the felspar or to hybrid material introduced. At other times it is clear except for kaolinisation, and is very much like the type which has developed from the hybrid magma. Occasionally reduction in grainsize has occurred.

Surrounding these remnants of solid dolerite are the minerals developed from the hybridised keratophyre. The composition of the plagioclase ranges from Ab_{91} to Ab_{99} , and is probably due to slight basification. Generally, however, these minerals are similar to those described as the keratophyre (see p. 165).

(iii) Veins and Other Late-Stage Phenomena.

In all the hybrids, particularly in the spotted types, irregular patches (<1 mm. to >3 mm. across) consisting of albite, clinozoisite, epidote (sometimes with allanite), quartz, and occasionally calcite are developed. When only small quantities of solutions were available these minerals were deposited in the interstices; when large quantities were present, replacement of the earlier-formed minerals occurred. The potential epidote molecule was the most active and selectively replaced both felspar and ferromagnesian minerals. The albite molecule at this stage played but little part in replacement and gave rise to albite in the interstitial areas.

Where carbonates occur they form irregular masses associated with the altered ferromagnesian minerals, or fill cracks in the felspar and sometimes partially replace the latter mineral.

The allanite is associated with the yellow epidote and forms either groups of radiating crystals which sometimes fill interstices, or prisms up to 0.5 mm. long. Twinning is occasionally shown and zoning is well marked with a dark core which shows signs of corrosion. It is a golden brown colour, X=light brown, Y and Z=deep reddish brown, $X \wedge c = 33^\circ$, $\gamma' - \alpha' = 0.021$, orientation negative, and the optical character is indefinitely positive (Fig. 4 A-D).

Where there were still greater quantities of solutions, concentration into cracks, probably produced as a result of cooling, took place. Thus in different parts of the intrusion, epidote, epidote-albite, quartz-epidote-albite, and quartz-epidote veins were formed. The epidote veins range in width from 0.05 to 3 mm. and consist of epidote and clinozoisite. In the larger ones radiating intergrown crystals occur and in the smaller the minerals are granular.

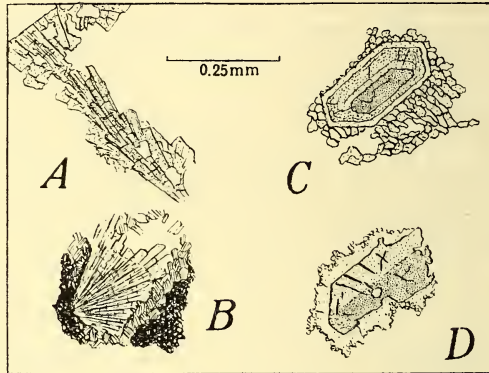


Fig. 4. Allanite.

- A. Allanite (heavily stippled) and epidote showing a parallel, radiating arrangement in an interstice.
- B. In this interstice a fibrous radiating mass of allanite terminates in small well-formed epidote crystals.
- C. A zoned crystal of allanite surrounded by granular epidote.
- D. A twinned crystal of allanite surrounded by epidote.

The epidote is yellow and markedly pleochroic, with a sporadic separation of iron which leaves it bleached and more like clinozoisite. At times a parallel arrangement of veins is shown, and dislocation of the plagioclase laths indicates that the veins are true displacement types. The larger ones have irregular boundaries and are at least partially chemical replacement types, although the original position may have been determined by fracturing (Fig. 5 A). Hereafter they will be referred to as replacement veins.

Albite-epidote veins are rare, and consist of a hypidiomorphic granular rock which is medium grained. The feldspar is most commonly in tabular crystals, but is sometimes granular. Chequer-albite is also fairly commonly

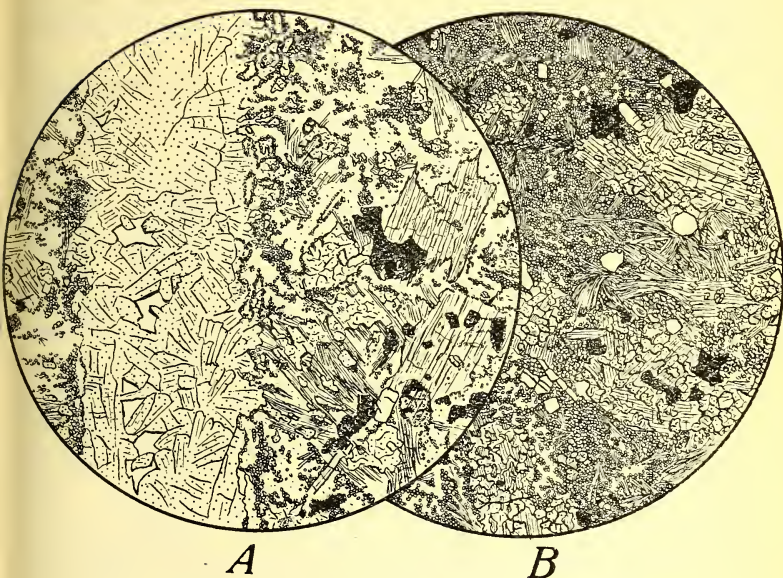


Fig. 5. Types Produced by Late Hybridisation Processes.

- A. The epidote vein is largely a chemical replacement type penetrating a hybridised dolerite. Along the edges of the vein epidotisation of felspar has taken place and a few large patches of epidote are found. The uralitised augite is only slightly attacked. Ilmenite is replaced by sphene and some fibrous actinolite has developed. $\times 13$.
- B. A portion of a hybridised dolerite in which epidotisation has been carried almost to completion. The felspar is almost entirely altered and the uralite shows replacement by larger grains of epidote. Much actinolite has developed. The apatite is the grey variety and belongs to the original diorite. $\times 13$.

found, sometimes surrounding the more normal type. The epidote is yellow and pleochroic and has either an interstitial or an ophitic habit, while it occasionally fills cracks, indicating that it crystallised fairly late (Fig. 6 B). Considerable quantities of ilmenite are present with white borders of leucoxene, together with a few tiny flakes of yellow pleochroic biotite, both of which appear to be incorporated from the surrounding rock. A green hornblende is found with increasing development towards the edge of the veins; this is described below (see pp. 176-7). In the centre of the vein it forms long needle-like crystals, up to 1 mm. in length, which are often grouped into

sheath-like bundles; near the edge a hornblende-albite rock is developed, in which the former mineral occurs in fibrous masses (Fig. 6 C).

Quartz-epidote veins are fairly common, and range from 0.1 mm. to 15 mm. in width. They seem to be mainly displacement-veins filling already formed cracks, and the larger ones contain fragments of felspar from the surrounding rocks. The epidote forms prisms up to 2 mm. long in the larger veins and is granular in the smaller ones. The quartz sometimes occurs in slightly elongated grains, oriented so that their long axes are parallel. This would indicate that the veins have been sheared and are therefore pre-granite in origin. Quartz-epidote-albite veins occur in places, but they resemble the quartz-epidote types, except that the felspar is present in very small amount.

The introduction of these veins gives rise to much the same mineralogical changes in the surrounding rock as those already mentioned in connection with the interstitial solutions. First, the plagioclase of both doleritic and hybrid origin is replaced by granular masses of epidote. Along the edges of the vein complete epidotisation of felspar may take place, but further away it becomes gradually less intense, taking place only along cleavage cracks (Fig. 5 A). With more profound epidotisation all the felspar is replaced and the uralite is also attacked and replaced by slightly larger, more intensely pleochroic grains of epidote, indicating an addition of iron from the uralite. At this stage there appears a fine fibrous green amphibole which may be fairly closely associated with the replaced hornblende, or may develop in what is now completely altered felspar (Fig. 5 B). As already stated it is found along the edges and even towards the centre of the albite-epidote veins, and also in areas where there has been chemical replacement around interstices. It is

Fig. 6.

- A. Part of a zone of apatite crystals produced in one of the spotted hybrids a short distance from an invading keratophyre vein. The crystals tend to be elongated parallel to the length of the vein. $\times 13$.
- B. An Albite-Epidote Vein. The albite is in rather tabular crystals and the epidote is largely interstitial. Actinolite is present as small acicular crystals. $\times 13$.
- C. The edge of the albite-epidote vein B, showing masses of fibrous actinolite crystals (including several cross sections) associated with albite and ilmenite. $\times 13$.

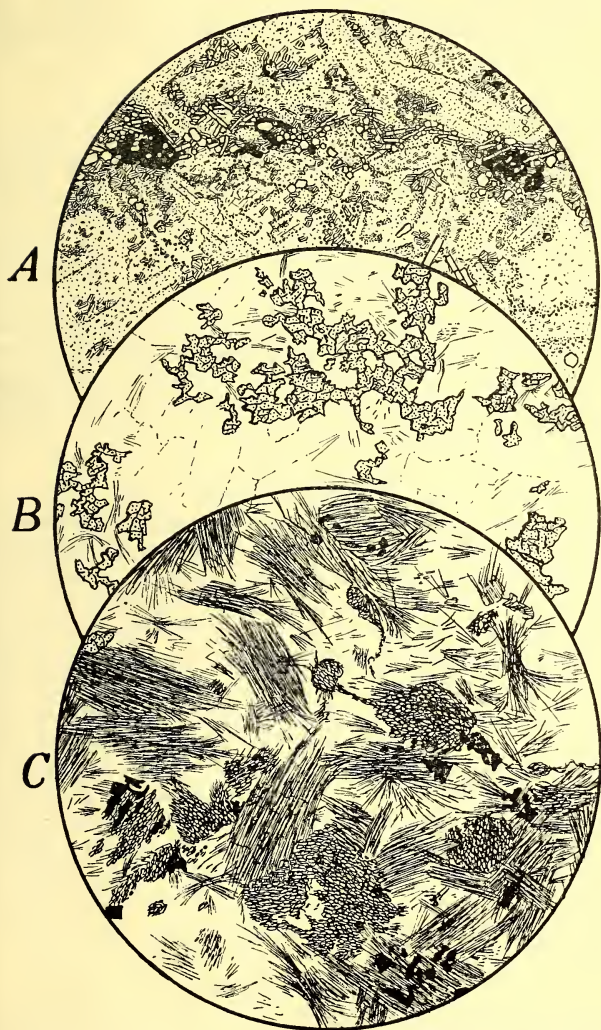


Fig. 6.

optically negative, with positive elongation, $Z \wedge c = 19^\circ$, $\alpha' = 1.626$, $\gamma' = 1.652$. Pleochroism is very marked: X=light yellow, Y=brownish green, Z=bluish green, $X < Y < Z$, which indicates that it belongs to the actinolite group.

(iv) Dynamically Metamorphosed Types.

The results of shearing are evident in all the rock-types in the north-western part of the area (see map). The direction of schistosity is N. 65° W. Away from this zone of definitely schistose rocks less intense movement is indicated by localised strain, which has produced small elongated patches of very clear recrystallised felspar and quartz, in which the associated biotite flakes show a parallel arrangement. Generally the plagioclase is somewhat contorted and may show slight clouding (MacGregor, 1931). Since all three main types have been influenced by dynamic changes it is obvious that both intrusions took place prior to the faulting.

(a) Keratophyres.

These rocks appear to have contained considerable quantities of dispersed xenoliths and are most likely hybrid types. The plagioclase, much of which is of doleritic origin, has not been completely recrystallised, shows "nibbled" edges, and contains a few granules of epidote and clinozoisite and dust-like inclusions, probably of iron ore. The surrounding material, which probably represents the original keratophyre magma, has recrystallised to tiny grains of quartz, plagioclase, which is sometimes finely twinned, and orthoclase. The biotite is in very tiny, slightly greenish flakes and shows the normal straw-yellow to brownish grey pleochroism. These have been segregated into long wavy, string-like masses, associated with finely granular ilmenite (Fig. 7 A). At times these have been forced to wrap round the remnants of felspar crystals and give the rock a slightly augen structure.

(b) Spotted Hybrids.

The spots shown in the unsheared types are still preserved but they are rather elongated (Fig. 7 B). In the field these rocks are further from the zone of stress and show less schistosity than the dolerites. Much of the biotite is of a colour similar to that in the above types but is in larger flakes. It is closely associated with finely granular

quartzofelspathic material and shows a parallel arrangement. Remnants of yellow epidote and hornblende remain, but the latter is mostly altering to biotite. The felspar crystals from the original dolerite show either recrystallisation round the edge, or "nibbling", while others have been bent or broken with the formation of clear untwinned bands across them. Apatite and masses of ilmenite, usually accompanied by sphene, show either bending or considerable fracturing.

(c) Dolerites.

The dolerites show intense shearing and in hand specimen could be called biotite-schists. The microscope, however, reveals fairly considerable quantities of hornblende of metamorphic origin and the rock is more truly a hornblende-biotite-schist.

The plagioclase is much more recrystallised than in the previous types, its shape having been obliterated, and only a few rounded masses 1 mm. to 1.5 mm. remain, surrounded by granular material. Epidote and clinozoisite, so noticeable in many of the hybrids, are not found, but many tiny rounded flakes of green biotite or minute fibrous and radiating needles of hornblende have developed. The recrystallised colourless material is composed of quartz and plagioclase.

The alteration of the uralitised ferromagnesian mineral shows some variation. Often a crystal is broken into as many as three pieces, and along the shear-planes biotite has developed. Masses of small actinolite crystals are developed about the uralite crystals, usually elongated parallel to the direction of schistosity. Aggregates formed in this way give a somewhat poikiloblastic appearance to the rock. Where orange-brown biotite occurs only between the fibrous uralite crystals it may have developed during previous hybridisation. However, where biotite forms large masses, it would seem to be of metamorphic origin, and at times biotite develops along one side of a mass of uralite and actinolite along the other (Fig. 7 C).

As in the previous type elongated flakes of biotite are segregated into irregular bands and patches, often in conjunction with magnetite and ilmenite which has been segmented and surrounded by sphene. The colour of the biotite ranges from pale greenish yellow to bright orange-brown; pleochroism of the former is X=pale straw yellow, Y=greenish grey, Z=greenish brown, and of the latter

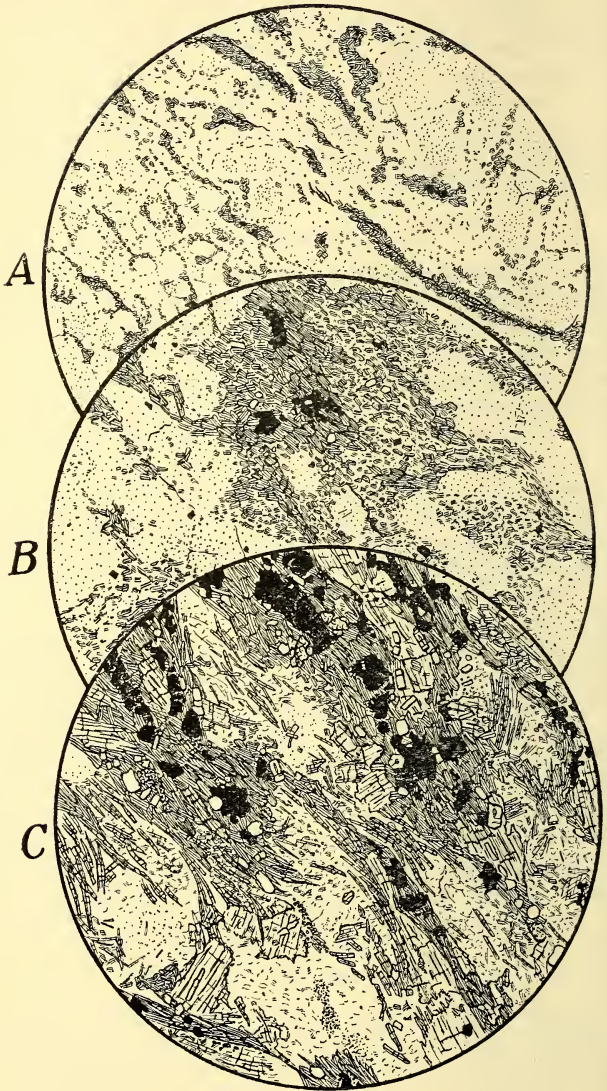


Fig. 7.

X=bright straw yellow, Y=reddish orange, Z=bright orange; for both $X < Y \leq Z$.

The metamorphic hornblende forms small elongated prisms which are often grouped into large aggregates (2 mm. long), but minute needles form radiating aggregates. This amphibole shows marked cross-parting, is bluish green, with strong pleochroism. X=greenish yellow, Y=yellow-green, Z=deep blue-green $X < Y < Z$; elongation negative, optical character positive, $Z \wedge c = 17^\circ$. It is thus most likely an actinolitic variety. The apatite is broken along the cross-parting, separation sometimes being as much as 1 mm.

The outcrops near the mine dump in Por. 43, Par. Wuuluman, represent a type which contains no biotite and shows no directional structures. Fibrous green hornblende has replaced the original ferromagnesian minerals, and in the remnants of plagioclase and the surrounding recrystallised patches needles of the same hornblende have developed in great numbers. The needles in the plagioclase were probably produced as a result of clearing of the original feldspar such as is described by MacGregor (1931). Skeletal ilmenite shows great alteration to sphene.

Another unsheared type occurs a little north of the south-west corner of Por. 98, Par. Wuuluman, but it shows less recrystallisation than the type near the mine-dump. Here the original ferromagnesian minerals of the dolerite have been replaced by a fibrous green hornblende and occasional biotite flakes. The albitic plagioclase shows

Fig. 7. Dynamically Metamorphosed Types.

- A. Keratophyre. The criss-cross flakes of biotite have been arranged in clots and bands associated with limonite. Much recrystallisation of the feldspar is shown, remaining crystals showing irregular rounded edges. $\times 13$.
- B. Spotted Type. Although the spotted areas are still visible they are somewhat elongated and the biotite flakes show a parallel arrangement. (Contrast with 2, B.) The plagioclase crystals are cracked and strained and in places partially recrystallised. $\times 13$.
- C. Dolerite. This is now a hornblende-biotite-schist. The original uraltite is replaced by both biotite and actinolite (showing cross parting) often within the one mass—S.E. quadrant. Actinolite and biotite develop within the recrystallised feldspars. All minerals, including the masses of ilmenite, largely changed to sphene, show a parallel arrangement. The cellular apatite is much fractured and the segments separated. $\times 13$.

only slight signs of recrystallisation, but contains grey patches of minute grains of iron ore and occasionally hornblende (see p. 165).

4. PETROGENESIS.

(1) Mineralogical Transformations.

The foregoing petrological descriptions serve to indicate that there were two influxes of keratophyric magma, first, one rich in soda, and, secondly, one in which potash was more concentrated (see Table I). The second was responsible not only for the formation of biotite within the hybrids but also for the introduction of orthoclase into the sodic felspar of both the keratophyre itself and its hybrids.

The earliest change in the augite and hornblende of the original dolerite is the development of uralite, and at the same time green hornblende is precipitated from the hybrid magma. The uralitisation may, in part, be a metamorphic change, but generally seems to be a hybrid adjustment due to the introduction of a fluid magma low in the reaction series (Bowen, 1915). The presence of abundant volatiles probably made possible the development of hornblende in the hybrid magma.

Nockolds (1933) cites a number of examples to show that soda diffuses more rapidly than potash into a rock in which lime is more plentiful than magnesia, and it may be this fact which accounts for the early development of uralite in the hybrid dolerites, to be followed slightly later by biotite. This is borne out somewhat by chemical analyses. The change from uralite to biotite results in a further release of lime and at the same time the anorthite molecule is being released from the felspar. For a short period this increase in lime in the rather small quantity of solution introduced, together with iron probably released from the ilmenite-sphene reaction, seems to make possible the development of a more actinolitic hornblende as blue-green edges to masses of uralite and hornblende from the hybrid magma, which have not yet been replaced. Thus for a short time biotite and hornblende remain in equilibrium in the magma. With a slightly greater increase in the potash content of the invading solutions, there is a decrease in the proportion of lime contained, and all the hornblende is rendered unstable and is gradually replaced by biotite. Complete alteration is found only in the most acid of the spotted hybrids.

	Hybridised Dolerites.	Spotted Hybrids.	Hybridised Keratophyre.
<p>The Ferronmagnesian Minerals.</p> <p>The original Ferronmagnesian minerals.</p> <p>Precipitation from the hybrid magma.</p>	<p><i>Introduction of soda.</i></p> <p>Augite →</p> <p>Pale green Uralite.</p> <p>Hornblende →</p> <p>Accompanying these changes.</p> <p>Ilmenite → Sphene.</p> <p>The precipitation of green hornblende.</p>	<p><i>Introduction of potash also.</i></p> <p>Uralite → Biotite.</p> <p>Accompanying these changes.</p> <p>Ilmenite → Sphene and Biotite.</p> <p>Green Hornblende → Biotite.</p> <p>Actinolitic hornblende develops as borders to unaltered uraltic and hybrid hornblende.</p>	<p><i>With increase in soda and potash and therefore a decrease in lime.</i></p> <p>All hornblende → Biotite.</p> <p>Accompanying this change</p> <p>Ilmenite almost completely replaced by sphene and biotite.</p> <p>All hornblende → Biotite.</p>
<p>The Original Plagioclase.</p>	<p>Basic plagioclase albitised. Anorthite molecule removed. This may be precipitated as epidote from the hybrid magma.</p>	<p>Basic plagioclase albitised with the development of epidote and clinzoisite <i>in situ</i>.</p>	<p>As in spotted hybrids.</p>
<p>Mechanical Introduction of Keratophyre Solutions.</p>	<p>Slight separation of plagioclase laths and the formation of rims of albite.</p>	<p>Wider separation and the formation of "pools" of keratophyre material. Generally injection is peaceful, but occasionally strewing of biotite flakes results.</p>	<p>More injection and considerable strewing results in the development of dark coloured spots.</p> <p>Complete disintegration of included xenoliths.</p>
<p>Veins and Late Stage Phenomena.</p>	<p>Introduction and/or concentration of epidote-bearing solutions which may replace plagioclase and the ferromagnesian with the release of MgO. This makes possible the development of actinolite which is often associated with the epidote.</p>		<p>Small quantities of epidote are found in interstices.</p>

The original basic plagioclase has been almost completely albitised and around these cores new albite has been deposited from the first soda-rich magma invasion. The fate of the released anorthite molecule is variable. So far as the plagioclase is concerned it is either removed or deposited as clinozoisite and epidote. When removed into the hybrid magma it is stored up until its saturation-point is reached. This may occur while the rock is still largely liquid. However, it is more usual for the anorthite molecule to remain in solution until the rock is partially consolidated, when it takes part in late hybridisation changes. The formation of epidote, clinozoisite, and albite in zones in the plagioclase may be due to hydrothermal metamorphism during the early stages of the injection of keratophyre solutions, or to the direct result of hybridisation. Where sericite is found to the exclusion of albite it seems most likely to be a hybrid change. In the Dhoon granite, Nockolds (1931) has a rather similar association, which he has attributed to the fact that the feldspar could not react quickly enough and ceased to be in equilibrium, with the result "that the soda more or less completely replaced the lime, which was thrown out as zoisite". Laitakari (1918) and Eskola (1921, 1922) conclude that in a low-temperature environment with an abundance of water, albite and epidote will arise rather than a more basic plagioclase. At Ben Bullen, Joplin (1935) finds a similar association due to the assimilation of lime. At Wuuluman the highly sodic aqueous magma probably prevented the formation of plagioclase, in which case the reaction was closely related to that indicated by Nockolds, Laitakari, and Eskola. These alterations brought about by sodic solutions closely resemble deuteric alterations; in this case, however, they are not residual liquors of a crystallising rock-mass but are related to a later intrusion.

There is much evidence available to show that after a considerable amount of hybridisation had taken place the rocks were subjected to further alteration. This took the form of intense epidotisation of feldspar, of uralite, and, to a smaller degree, of biotite. It was brought about by solutions trapped in interstices in the almost consolidated rock and also by veins, the positions of which were probably determined by cooling-cracks, although considerable chemical replacement is found along the edges of the larger ones. Clinozoisite and allanite accompany the

epidote. The soda at this stage was rather inactive. These solutions evidently represent the last remnants of the keratophyre magma modified by the addition of material from the dolerite, chiefly lime and iron derived from the different hybrid reactions. This intense epidotisation released considerable quantities of magnesia from the ferromagnesian minerals, which united with the potential epidote molecule, and possibly some of the potential albite molecule, to form the fibrous actinolite, found where intense alteration has taken place and along the edges of the larger invading albite-epidote veins. The development of this amphibole at a time when the rocks were largely consolidated and considerably cooled must have been made possible by the presence of volatiles which were undoubtedly present.

(ii) Chemical Discussion.

For the purpose of comparison the analyses I-V of Table II have been recalculated so that equal volumes may be compared. There is considerable difference in density between the original altered dolerite and the hybrid types; the slightly hybridised dolerite is 1.34% denser, the hornblende-biotite spotted hybrid 4.36% less dense, and the biotite-rich spotted type 6.04% less dense. The first has therefore been recalculated to approximately 100.91% and the other two to 95.86% and 93.52% respectively. The altered dolerite and the keratophyre have been recalculated to 100% (see Table III).

Compared with the original altered dolerite the hybrids generally show a marked decrease in iron, MgO, CaO, TiO₂ and MnO, and an increase in Na₂O, K₂O, SiO₂ and P₂O₅. The position of Al₂O₃ is somewhat variable. With the exception of number two there is a steady increase in the Na₂O/K₂O ratio as the dolerite is approached, possibly due to the excess of lime over magnesia (Nockolds, 1933).

The keratophyre has not been compared with the hybrids, as all specimens show signs of assimilation and its original composition is not known.

It has been shown that augite is first replaced by hornblende and later this is replaced by biotite, also the originally basic plagioclase is replaced by albite, often with the removal of the anorthite molecule. Nockolds (1935) has shown that the nature and amount of material introduced from the hybrid magma, and subtracted from the

TABLE II.

	I.	II.	III.	IV.	V.	VI.
SiO ₂ ..	49.79	50.21	56.52	58.20	64.27	46.73
Al ₂ O ₃ ..	18.63	19.53	19.47	20.43	17.33	18.73
Fe ₂ O ₃ ..	1.46	0.90	3.16	0.35	2.65	nt. fd.
FeO ..	8.12	8.03	3.57	4.17	2.04	10.14
MgO ..	5.67	4.54	1.92	1.77	0.85	3.56
CaO ..	9.31	9.03	5.09	3.34	0.91	8.62
Na ₂ O ..	3.54	2.25	5.57	5.86	5.52	3.54
K ₂ O ..	1.09	2.29	2.20	3.41	5.01	0.88
H ₂ O+ ..	0.86	1.14	0.61	0.59	0.34	3.31
H ₂ O- ..	0.06	0.05	0.09	0.08	0.09	0.35
TiO ₂ ..	1.15	1.13	0.94	0.85	0.49	2.74
P ₂ O ₅ ..	0.17	0.29	0.93	0.44	0.16	0.37
MnO ..	0.17	0.18	0.15	0.07	0.09	0.37
CO ₂ ..	—	—	—	—	—	0.58
FeS ₂ ..	—	—	—	—	—	0.05
Total ..	100.02	99.57	100.22	99.56	99.75	99.97
Sp. Gr. ..	2.98	3.02	2.85	2.80	2.69	—

- I. Altered Dolerite, South of road in Por. 43 Par. Wuuluman. Anal. E. M. Basnett.
- II. Slightly hybridised Dolerite. Por. 111, Par. Wuuluman. Anal. E. M. Basnett.
- III. Spotted Hybrid containing Hornblende. Just east of north-south road, Por. 69, Par. Wuuluman. Anal. E. M. Basnett.
- IV. Spotted Hybrid rich in Biotite. Towards eastern boundary, Por. 99, Par. Wuuluman. Anal. E. M. Basnett.
- V. Keratophyre. On top of hill, Por. 69, Par. Wuuluman. Anal. E. M. Basnett.
- VI. Albite-Diabase. Trusham Station Quarry, west side of Teign, Devon. Anal. E. G. Radley. *Geol. Mag.*, 1911, p. 208.

xenoliths, will vary with the rate at which the different reactions take place. Small quantities of MgO are set free in the ferromagnesian changes, and CaO is also released, but much more abundantly in the change from hornblende to biotite. The release of these two constituents from the original ferromagnesian mineral enables the hornblende to develop from the hybrid magma, and probably accounts for the development of a more actinolitic variety when the

TABLE III.

	I.	II.	III.	IV.	V.
SiO ₂ ..	49.78	50.90	54.05	54.68	64.43
Al ₂ O ₃ ..	18.62	19.79	18.62	19.20	17.37
Fe ₂ O ₃ ..	1.46	0.92	3.02	0.33	2.66
FeO ..	8.12	8.14	3.41	3.92	2.05
MgO ..	5.67	4.60	1.84	1.60	0.85
CaO ..	9.31	9.15	4.87	3.14	0.91
Na ₂ O ..	3.54	2.28	5.33	5.51	5.54
K ₂ O ..	1.09	2.32	2.10	3.20	5.02
H ₂ O+ ..	0.86	1.16	0.58	0.55	0.34
H ₂ O- ..	0.06	0.05	0.09	0.09	0.09
TiO ₂ ..	1.15	1.15	0.90	0.80	0.49
P ₂ O ₅ ..	0.17	0.29	0.89	0.41	0.16
MnO ..	0.17	0.18	0.14	0.07	0.09
	100.00	100.93	95.84	93.50	100.00

I. Altered Dolerite recalculated to 100%.

II. Slightly hybridised Dolerite recalculated as explained in text.

III. Spotted Hybrid containing hornblende recalculated as explained in text.

IV. Spotted Hybrid rich in Biotite recalculated as explained in text.

V. Keratophyre recalculated to 100%.

change from uraltite to biotite first takes place. The iron and titania for the formation of biotite probably arise from the break-down of ilmenite, while lime is used for the formation of sphene. The formation of hornblende or biotite depends probably on the K₂O content, and possibly also upon the amount of available water. The greater part of the CaO is stored up until late in the hybridisation history. It must also be remembered, however, that in all these types solutions, as such, have entered the hybrid rocks to a considerable degree, and so there has been an actual mechanical addition. The increase in P₂O₅ in the hybrid types is shown in the formation of large quantities of apatite needles within the xenolithic spots and from the hybrid magma itself, the lime being supplied by the reactions already discussed. The presence of much apatite and of small quantities of tourmaline and of pyrites in the hybrid rocks indicates that considerable quantities of

volatiles have been introduced, and these have undoubtedly been derived from the keratophyre magma.

(iii) **Physical Conditions of the Invading Magma.**

In the Wuuluman Creek Intrusion we are not only dealing with a number of xenoliths which have been incorporated in a fluid magma, but also with a rock-mass which has been saturated with keratophyre solutions giving rise to a considerable mass of hybrid rocks.

It is evident from the development of albite and epidote in the basic plagioclase, the formation of epidote veins, and the abundance of apatite, that the invading keratophyre contained considerable quantities of volatiles and was at a relatively low temperature. It seems most likely that the amount of penetration which has taken place could have been possible only if the dolerite itself still retained some heat. Again, as already stated, it seems likely that the keratophyre magma did not penetrate to the surrounding sedimentary rocks, so that whatever heat and volatiles it originally contained would be dissipated more slowly.

The alteration of the original minerals of the dolerite, particularly the ferromagnesian types, would suggest a diffusion of material into the dolerite in advance of the magma, to be followed later by actual mechanical injection. When in small quantities this was rather peaceful, but as the quantity of injected material became greater considerable movement occurred. It was not always related to the amount of material introduced as considerable disintegration is found in the hybrid dolerites.

5. SUMMARY.

The Wuuluman Creek mass has been shown to consist of two separate intrusive types. The younger, a keratophyre, has invaded an earlier mass of dolerite and has produced zones of hybrid rocks.

The mineralogical changes in the hybrid rocks have been shown to be due to the introduction of sodic keratophyre magma, followed by the injection of a keratophyre magma richer in potash. Later changes were brought about around veins and interstices which were filled with solutions containing material released during the hybridisation of the dolerite. The constant development throughout the hybrids of albite and epidote, instead of a more basic feldspar, is considered to be due to low temperature conditions and to an abundance of water.

Some time after consolidation the north-western part of the mass was subjected to dynamic metamorphism, probably as a result of faulting, and the rock types produced have been described.

Recalculated analyses have been made the basis for the consideration of reciprocal reaction in so far as such a discussion is possible.

6. ACKNOWLEDGMENTS.

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INFRA-RED RADIATIONS AND THEIR QUENCHING
EFFECT ON ZINC-SULPHIDE PHOSPHORS. II.*

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(With Plates VII-X.)

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ABSTRACT.

After a brief reference to his "Shift of spectral distribution effect" and the "Intensification" of phosphorographs by heat (with which he dealt in a previous paper)* the author proceeds to describe further investigations. Details are given of a method of phosphorographic "reduction" by lowering of temperature. It is also shown experimentally that at any given temperature over a wide range, a photographic image can be imprinted by light upon a Zn S-Cu screen. This energy picture can be "frozen-in" or suspended for any length of time if the temperature is lowered sufficiently, and will return unimpaired when the screen is allowed to recover its original temperature level.

A series of phosphorographs illustrate the fact that, having "frozen-in" one image, a second one may be applied to the frozen screen, and this also can be "frozen-in". As the screen progressively recovers heat these images reappear, each at its original temperature level. This provides a method for identifying various selected temperature levels, which may find application in further researches into the properties of phosphors.

It is shown that at low temperatures, infra-red radiations still cause quenching of phosphorescence, but the process is retarded. Use is made of this slowing down to study the increased luminosity which momentarily precedes quenching at ambient temperature. It is shown by experiment that both of these effects (increased luminosity and quenching) are due to the same wave lengths. It is demonstrated that

* The previous paper appeared THIS JOURNAL, 1939, 73, 112-124.

+ or -3° C. of temperature change can be detected visibly by means of a zinc sulphide screen. The results of some experiments with zinc sulphide and calcium sulphide phosphors at -183° C. are described. Improvements in phosphorographic technique are indicated, and applied by the author to the taking of infra-red spectrographs. The joint work of the author and N. R. Hansen is described in the measurement of the wave-lengths responsible for energizing and quenching. Spectra and curves are given. The author's method of making phosphorescence decay curves is described, and a curve is given for Zn S-Cu at 19.5° C. An instrument is described and illustrated for locating and measuring the shift of the "neutral point" between the energizing and the quenching radiations under various conditions. The possibility of employing zinc sulphide screens for "spark photography" is investigated and the results are given. By means of a special apparatus described in the paper, a comparison is made between zinc sulphide screens and photographic plates with regard to their respective responses to visible light reflected from various coloured surfaces. Photographs are reproduced which show that a \odot Zn S screen behaves in a similar manner to a very slow plate.† The response of \times Zn S to infra-red radiation as reflected from various coloured surfaces is shown to be the same for all colours. The response of \times Zn S to red light is relatively the same as that of a panchromatic plate, except that the latter is faster.

In a previous paper before the Royal Society of New South Wales¹ the author demonstrated his "Shift of spectral distribution effect". A variable resistance "A C", Plate VIII, Fig. 9, was connected in series with a 100 W. metal filament lamp L. A Zn S-Cu screen² was energized by exposure to the lamp, whilst a sliding contact B was set at an optional position, say midway between A and C. A finished photographic negative was

† The two symbols employed above and throughout this paper denote :

- \odot That the phosphor has not been exposed to an energizing radiation.
- \times That the phosphor has been excited to phosphorescence.

¹ THIS JOURNAL, 1939, 73, 120.

² For the manufacture of phosphor screens, see reference 1.

placed over the ✕ Zn S-Cu screen, which was then re-exposed to the lamp after the sliding contact had been advanced nearer to C. A phosphorescing "negative" resulted. It was also shown that when after energizing the screen at position B the sliding contact was moved back nearer to the end A of the resistance, a phosphorescing "positive" was produced.

The name "phosphorograph" was suggested by the author for contact prints from phosphorescing screens.

INTENSIFICATION OR REDUCTION BY CHANGE OF TEMPERATURE.

The author showed that the application of heat to a "phosphorescing picture" increased its luminosity and intensified the image.

As will be seen from a portion of the work embodied in the present paper, the picture upon a phosphorescing Zn S-Cu screen is reduced in intensity when the temperature of the screen is lowered. An example of this is shown in Pl. VIII, Fig. 7. This is an over-exposed phosphorograph, and the central portion has been "reduced" by placing the Zn S screen upon a "frozen" metal plate.

It was shown by the late Sir James Dewar that when a tube of phosphorescing calcium sulphide was immersed in liquid air its luminosity was inhibited, but returned as the screen recovered its original temperature. Since this experiment was performed most of the phosphors have been examined at low temperatures.³

LOW TEMPERATURE INVESTIGATIONS.

The following work was carried out in order to ascertain the effect of low temperatures upon zinc sulphide screens.

Suspended Phosphorescence.

A pencil of compressed CO₂ was pressed against the back of a ✕ Zn S-Cu screen, as illustrated in Pl. VIII, Fig. 8. A dark patch gradually developed due to the "freezing-in" of the phosphorescence. Contact was maintained between the screen and the CO₂ whilst the former was re-exposed to blue light. After the removal of the CO₂ the frozen portion glowed much more brilliantly than the rest of the

³ "Handbuch der Experimentalphysik," Band XXIII, by P. Lenard, E. Schmidt and R. Tomaschek, "Phosphoreszenz-Fluoreszenz," Leipzig, 1928.

screen, the explanation being that the unfrozen portion had reached a lower level on the phosphorescence decay curve before the frozen part had commenced to yield up its stored energy.

This experiment also shows that even in its frozen state the zinc sulphide is capable of storing up additional energy.

The Effect of Low Temperature Upon a Phosphorescing Photographic Image.

PL. VII, Figs. 1 to 12, is the reproduction of a series of phosphorographs taken at different temperatures and under various conditions, as under :

- (1) was taken at 17° C.
- (2) shows the same phosphorescing image after it had been placed between two blocks of compressed CO_2 snow for three-quarters of an hour, thus reducing its temperature to -78.2° C.
- (3) The same after a further two hours' freezing at -78.2° C.
- (4) The same when brought back to just below ambient temperature. Whilst this photograph was in process of development the screen was refrozen.
- (5) After it had been placed upon a plate of metal heated to 10° C.

The screen was then allowed to rest at ambient temperature for a further 30 minutes, by which time the image had practically disappeared by natural decay of phosphorescence.

- (6) is the same screen after its temperature had been increased by a further application of the heated metal plate.

In the case of phosphorograph 2, before the panchromatic plate was placed upon the screen, not a vestige of the image could be seen; it was completely frozen-in. That the right-hand side of the picture shows slightly in the phosphorograph is due to the difference in the relative temperatures of the panchromatic plate (17° C.) and of the Zn S screen (-78.2° C.). The plate had commenced to thaw out the screen.

The plate was acting as a heated plate would have done to a screen at ambient temperature. Reference will be made to this later in the paper under the heading of

“Improvements in photographic technique”. In order to confirm the complete disappearance of the photographic image in phosphorographs 2 and 3, after the screen had been frozen, markers in the forms of a small paper cross, and a narrow strip of black paper, were placed respectively between the screen and the panchromatic plate. If the frozen Zn S-Cu had been emitting light, in the comparatively long periods during which it was in contact with the panchromatic plates outlines of these markers would have appeared.

It was next decided to ascertain if it was possible to re-energize a frozen Zn S-Cu screen, i.e. would the zinc sulphide be capable of absorbing additional energy, and what would be the effect of a second exposure upon the suspended image?

- (7) was made at ambient temperature 15°C . at -78.2°C .
- (8) shows the result after the screen had been “frozen-in” at -78.2°C .; all phosphorescence was suspended.
- (9) The screen was maintained at -78.2°C ., whilst another photograph was imprinted upon it (by exposure to light), i.e. the small circular picture.
- (10) The temperature was then lowered still further by placing the screen between a couple of tinned-iron containers in which had been placed a mixture of CO_2 snow and ether. This “froze-in” the second picture.
- (11) The temperature of the screen was then raised again to -78.2°C ., and as seen in this phosphorograph, the small picture returned.

The screen was then placed upon a sheet of metal at ambient temperature (15°C .). As the former returned to this temperature, the small photograph increased greatly in intensity and the first photograph returned.

- (12) The screen was then placed upon a heated metal plate and the brilliance of both pictures was intensified. A comparison between this phosphorograph 12 and phosphorograph 7 shows intensification.

After an interval of two hours during which time the screen was kept in the dark at ambient temperature, both pictures had practically disappeared through the process of normal phosphorescent decay. A further application

of heat partially restored them both. The smaller was still the stronger. The phosphorograph of this is not reproduced.

Pl. VIII, Fig. 11 illustrates the method of "freezing-in" the phosphorescence of the Zn S-Cu screen.

It is evident that the picture had lost none of its brilliance during all these manipulations, neither did any injury to the screen take place. From this series of phosphorographs it would appear that for a screen frozen to -78.2°C . that temperature can be considered as the ambient temperature of the screen. Above and below -78.2°C . its behaviour is similar to that of an unfrozen screen above and below the normal temperature of the room. Further experiments described later confirm this, and show that the same law holds good for a very long way up and down the temperature gradient. The reappearance of each successive image at the temperature level at which it was originally imprinted should provide a useful method of identifying selected temperature levels and may find application in further researches into the properties of phosphors.

Quenching by Infra-Red Radiations at -78.2°C .

A \odot Zn S-Cu screen (at ambient temperature 15°C .) was first energized by exposure to blue light for ten seconds. The phosphorescence thus produced was "frozen-in" at -78.2°C . and maintained at this temperature. It was re-exposed to blue light for a further ten seconds; this caused a second phosphorescence. Whilst still frozen, a small marker of paper was placed on the screen. It was then exposed to infra-red radiations from a 100 W. metal filament electric lamp, through a thin ebonite filter. This irradiation quenched only that portion of the screen surrounding the marker.

Low Temperature Retardation of Quenching.

In his earlier paper on this subject₁ the author made reference to the momentary increase of luminosity of a zinc sulphide screen at the first impact of quenching radiation and of the difficulty there was in observing it under certain normal conditions. As will be seen from the following experiment, a lowering of temperature provides an excellent means of studying the effect at leisure and in detail.

Pl. VIII, Fig. 10A shows a \times Zn S-Cu screen, behind and in contact with which is a strip of "frozen" glass. The image of the filament of an electric lamp L was projected through an ebonite filter on to the screen by means of a suitable glass lens. Directly the infra-red radiation reached the zinc sulphide a luminous image commenced to form, reaching a maximum intensity in approximately three seconds. In a further three seconds the image had become blurred, and after eight seconds more no image was perceptible. The screen remained without any visible image after this for approximately 21 seconds, and then a dark image began to form, which gradually blackened over a period of 90 seconds. At this juncture the rays were cut off. Immediately the whole process speeded up, and in another ten seconds the image was quite three times as black. The author succeeded in securing a photographic record of both the luminous and of the quenched image. Pl. VIII, Fig. 10, is the actual photograph. It was taken as follows:

After the screen had been energized and frozen an exposure to infra-red rays was made and the black image Q was allowed time to form; the screen was then shifted to the right and another rapid infra-red exposure of approximately $2\frac{1}{2}$ seconds was made. A panchromatic plate was then placed in contact with the screen with as little delay as possible, and after one second the former was removed and developed.

It is interesting to note that the luminous and dark images so obtained are both in the same focus of the projecting lens, proving that both the luminosity and the quenching are attributable to the same wave-lengths.*

The Sensitivity of \times Zn S-Cu to Small Changes of Temperature.

A special screen was made upon a backing of thin black paper (specially selected). It was possible to detect a rise or fall of only three degrees above or below ambient temperature, when the warmed or cooled bulb of a thermometer was held in contact with the back of the screen. These figures depend largely upon the individual eyesight of the observer; others might be able to detect even smaller temperature changes.

* Reference to the author's first paper, Pl. III, Fig. 4, and Pl. V, Figs. H and I, will provide an interesting comparison.

Some Experiments with Phosphors at — 183 C.

A number of different phosphors were sealed into thin walled glass tubes. Two tubes of \odot Zn S-Cu (green) were selected. One, "A", was placed in liquid oxygen, and the other, "B", was used at ambient temperature. The frozen and unfrozen tubes were then exposed simultaneously to blue light for ten seconds, after which they were both plunged into liquid oxygen. After removal therefrom, as their temperatures gradually returned to normal the Zn S in the frozen tube "A" was the first to recover its luminosity, and even after a lapse of 35 minutes it still exceeded "B" in brilliance (this experiment was repeated).

A similar test with Zn S (having orange phosphorescence) yielded a similar result, differing only in accordance with its decay curve.

Low Temperature Experiment with Alkaline Earth Phosphor.

A tube containing mildly energized CaS (light blue) was frozen in liquid oxygen. Whilst still frozen one end of it was placed in a beam of (ebonite-filtered) infra-red rays. This irradiation caused it to become luminous.

IMPROVEMENTS IN PHOSPHOROGRAPHIC TECHNIQUE.

As a result of the knowledge gained from the series of phosphorographs, Pl. VII, Figs. 1 to 6, the author has been able to improve upon the original method which he employed.¹ It had already been noted when making phosphorographs at ambient temperature that it was most necessary to place the panchromatic plate on to the screen as soon as possible after the exposure had been made. Not only did the general intensity of the picture rapidly decay, as would be expected when working near to the commencement of the phosphorescence decay curve, but the image appears to soak in and lose sharpness in detail. After a few minutes it has the appearance of a picture that has soaked into a hectographic jelly. Pl. VII, Fig. 1, is a good example of a phosphorograph made under normal conditions at ambient temperature.

The phosphorograph seen in Pl. VII, Fig. 5, shows much more contrast, in spite of all the processes through which it has passed. The 10° rise above ambient temperature has brought back every bit of the lost detail. Another point noted by the author was that having intensified a phosphorescing image by placing the screen

upon a heated plate, the application of an unheated panchromatic plate, if of long duration, greatly reduced the brilliance of the luminosity of the screen and the sharpness of the image. In view of the foregoing, the following is a better procedure. In lieu of the heated metal plate placed beneath the screen, the panchromatic plate itself should be warmed ten degrees or more in order that it may be applied at a higher temperature than that of the screen. In this way the picture can be maintained at a high value of brilliance throughout the whole time of contact.

It was next decided to make some measurements in order to ascertain which wave-lengths were responsible for quenching ∇ Zn S. Professor Vonwiller suggested that a Zn S-Cu screen might be used in the Hilger infra-red spectrometer at the Physics Department. The author also wishes to express his thanks to Mr. N. R. Hansen of that department for his valuable help and for the considerable amount of work which he did in locating and measuring the required wave-lengths with that instrument.

MEASUREMENT OF THE WAVE-LENGTHS RESPONSIBLE FOR THE ENERGIZATION AND THE QUENCHING OF Zn S—Cu PHOSPHOR, AND THE METHOD EMPLOYED.

A ∇ Zn S-Cu screen was placed in the Hilger spectrometer in place of a photographic plate. By this means we were able to obtain a spectrum which not only covered the visible but also extended at both ends into the infra-red and the ultra-violet. Having projected the spectrum from a carbon arc on to the ∇ Zn S-Cu screen, we removed the latter and made a phosphorograph (or contact print) therefrom on to a panchromatic plate. The spectrum was on a very small scale, which rendered it difficult to make exact measurements. We decided therefore to place the phosphorescing spectrum in the focus of a camera fitted with a magnifying lens. On removal (in the dark) of the phosphorescing screen from the spectrometer, the phosphorescing impression of the spectrum was very clearly seen. However the emission of light from the screen was found to be insufficient (even with an exposure of several minutes) to supply a useful photographic record; see Pl. X, Fig. 1A. Making use of the procedure described under the last heading in this paper, i.e. "Improvements in phosphorographic technique", a sheet of glass heated to about 100° C. was placed in front of the screen (of course

in contact with its phosphorescing surface). Plate X, Fig. 1B, shows the result obtained. As is seen thereon, there are three bands of wave-lengths which produce important energization of the Zn S-Cu; the head of each band is clearly defined at 0.36μ , 0.39μ , 0.43μ .

Quenching takes place over a continuous spectrum between 0.5μ and 1.0μ . There is a gap in this spectrum between 1.0μ and 1.5μ . This may be owing to insensibility of this phosphor to a small band of wave-lengths in this region. After this there is another very marked response to quenching at 1.5μ ; this band would appear to accord with the curves shown in Pl. X, Fig. 2, which we obtained for a 100 W. metal filament electric lamp focused on to the slit of the spectrometer by means of the identical glass lens employed throughout the author's earlier experiments.¹ These measurements are also in close accord with figures given by Le Bon⁶ for the infra-red quenching radiations from his paraffin lamp, to which black glass and ebonite are transparent, i.e. from 0.8μ to 3.0μ . Referring once more to the spectrograph, Pl. X, Fig. 1B, it is interesting to note that almost all the energization (phosphorescence) is produced by the flame of the arc, and most of the quenching by the heated electrodes. This is in accordance with the Bunsen flame experiments described by the author in his first paper¹ (page 120), where in order to obtain quenching radiation it was found necessary to place a piece of wire or other solid body in the flame and raise it at least to red heat.

CURVES OF PHOSPHORESCENT DECAY.

Decay curves have been made from time to time by various workers, of most if not of all the known phosphors. In most cases the rate of decay follows an exponential law.^{3 4} Pl. VIII, Fig. 3, is a decay curve made by the author for zinc sulphide, copper activated.

Incidentally it is most necessary to know not only at what temperature the decay curve is made, but also to maintain the same temperature throughout the process.

Making Decay Curves (the Author's Method).

Pl. VIII, Fig. 1, shows the apparatus. On the underside of the slider "S" and at the position indicated, a broad

⁴ "Fluorescence and Phosphorescence," E. Hirschlaff. Methuen and Co., London, 1938. Also *Journal of Franklin Institute*, 225, May, 1938, pp. 527-547 (for calcium sulphide curves).

line of Zn S-Cu (or other phosphor for which a curve is to be made) is painted. A panchromatic plate "P" is placed film upwards in the hollow space which is provided for it in the base "I". When the slider "S" is moved towards the right in a similar manner to that employed with a slide rule, the zinc sulphide line is moved across and just in contact with the photographic plate. A pawl controlled by a spring (as shown in the top right-hand inset of Pl. VIII, Fig. 1) presses down lightly into the spaces between the teeth of a suitable "rack" fitted in the base "I". This is indicated by dotted lines in the figure.

As the slider "S" moves from tooth to tooth across the rack, the phosphorescing line of zinc sulphide moves in similar stages over the surface of the panchromatic plate. When making a curve this Zn S line is first energized by exposure to a 100 W. electric lamp for ten seconds at a distance of ten inches. The slider is immediately pulled across to the right so as to bring the line into its first position across the left-hand end of the plate. It is allowed to rest there for ten seconds, then it is moved to the next position as determined by the rack and pinion, and retained there for ten seconds. At its next position it is allowed to rest for thirty seconds. After that it is moved to the fourth position and another ten seconds rest is made, and so on at prearranged intervals until it has traversed the length of the plate, always making rests of ten seconds duration between the longer periods. When the plate has been developed it is seen to be covered by a series of equidistant lines of diminishing density. Such a plate is seen in Pl. VIII, Fig. 4; this was the actual plate from which the curve seen in Pl. VIII, Fig. 3, was made; the twelve ten seconds rests are numbered above this photograph.

The finished plate is placed upright in the groove in the slider "S" and is fastened by adhesive tape to the angle bracket "Q". The whole arrangement is then screwed down firmly to the table or bench in the position indicated by the left-hand inset, Pl. VIII, Fig. 1, in such a manner that as the slider "S" is moved from tooth to tooth across the rack the ten seconds exposure lines on the plate always cover the slit shown in the shield "M". Light from an electric lamp or other source is focused through the plate and on through the slit on to a photo-electric cell in the galvanometer circuit. The readings on the scale of the



1. $ZnS-Cu$ SCREEN EXPOSED TO BLUE LIGHT FOR 5 SECS. CONTACT-PRINT ON PANCHROMATIC PLATE 9 SECS. TEMPERATURE $17^{\circ}C$. THE SCREEN WAS THEN FROZEN WITH CO_2 SNOW FOR $\frac{1}{2}$ HOUR & WHILST STILL FROZEN A PAPER CROSS (NOT SEEN IN PHOTO) WAS PLACED ON IT (SEE FIG 2)



2. WHILST STILL FROZEN A PANCHROMATIC CONTACT PRINT WAS MADE EXPOSURE 60 SECS. FREEZING OF SCREEN WAS CONTINUED DURING DEVELOPMENT. A STRIP OF BLACK PAPER WAS THEN LAID ACROSS THE SCREEN WHILST STILL FROZEN (FIG 3)



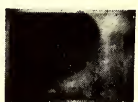
3. ANOTHER PANCHROMATIC CONTACT PRINT WAS MADE EXPOSURE 120 SECS. AFTER THIS THE SCREEN WAS KEPT FROZEN FOR A FURTHER 2 HOURS, IT WAS THEN PLACED UPON A HEATED COPPER PLATE. FOR THE RESULT (SEE FIG 4)



4. WHEN THE PICTURE HAD RETURNED A 9 SECS CONTACT PRINT WAS MADE ONTO ANOTHER PANCHROMATIC PLATE. WHILST THIS WAS DEVELOPED THE SCREEN WAS FROZEN AGAIN WITH CO_2 SNOW ($-78^{\circ}C$). IT WAS THEN PLACED UPON THE HOT-PLATE UNTIL IT WAS 10°



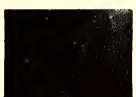
5. ABOVE AMBIENT TEMPERATURE (IT WAS THUS INTENSIFIED) A CONTACT PRINT WAS THEN MADE ON A PANCHROMATIC PLATE EXPOSURE 20 SECS. THE SCREEN WAS THEN LEFT AT AMBIENT TEMPERATURE FOR 30 MINS UNTIL



6. THE IMAGE HAD ALMOST FADED (BY NORMAL DECAY). IT WAS THEN REPLACED ON THE HOT PLATE & AN EXPOSURE OF 40 SECS PRODUCED PLATE G



7. A PHOSPHOROGRAPH WAS MADE ON A $ZnS-Cu$ SCREEN AT AMBIENT TEMPERATURE $15^{\circ}C$ WITH BLUE LIGHT. THE IMAGE WAS THEN FROZEN IN BY PLACING THE SCREEN BETWEEN 2 BLOCKS OF CO_2 SNOW. (SEE FIG 8)



8. WHILST STILL FROZEN THE SMALL PHOTO WAS PRINTED BY BLUE LIGHT ONTO THE $ZnS-Cu$ SCREEN. ITS TEMPERATURE WAS THEN REDUCED STILL FURTHER BY PLACING IT BETWEEN 2 TINNED-IRON CONTAINERS.



9. FILLED WITH CO_2 & AETHER THIS FROZE IN THE SMALL PHOTO. BOTH PICTURES WERE NOW FROZEN IN. (SEE FIG 10)



10. THE TEMPERATURE OF THE SCREEN WAS THEN INCREASED TO $-78.2^{\circ}C$ BY PLACING IT BETWEEN 2 BLOCKS OF CO_2 SNOW. THE SMALL PICTURE RETURNED (FIG 11). THE SCREEN WAS THEN PLACED UPON A BRASS



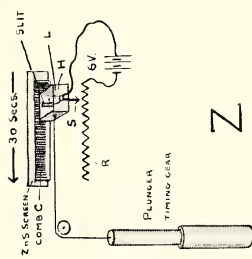
11. PLATE (AT AMBIENT TEMPERATURE) AS IT APPROACHED THE TEMPERATURE OF THE PLATE. THE SMALL PHOTOGRAPH INCREASED IN INTENSITY AND THE FIRST PICTURE RETURNED. THE SCREEN WAS THEN



12. HEATED ON A HOT-PLATE OF BRASS WHICH INTENSIFIED THE IMAGES AFTER WHICH PHOSPHOROGRAPH 12 WAS MADE. 2 HOURS LATER WHEN BOTH PICTURES HAD ALMOST FADED OUT HEAT PARTIALLY RESTORED THEM AGAIN. THE SMALLER WAS STILL THE STRONGER.

SPECTRAL DISTRIBUTION.

SHIFT OF NEUTRAL POINT, BETWEEN ENERGIZING & QUENCHING RADIATIONS.



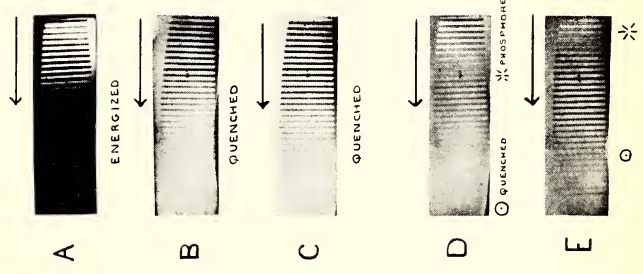
○ ZnS-Cu SCREEN EXPOSED TO 6V. TRAVELLING LAMP (UNFILTERED).

* ZnS-Cu SCREEN (STEEL ARC ENERGIZED), EXPOSED TO 6V. TRAVELLING LAMP THROUGH BLACK GLASS FILTER

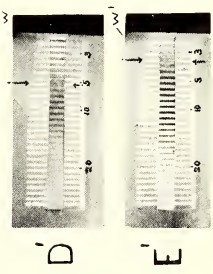
* ZnS-Cu SCREEN (STEEL ARC ENERGIZED) EXPOSED TO 6V. TRAVELLING LAMP (UNFILTERED)

* ZnS-Cu SCREEN ENERGIZED BY 6V LAMP AT SETTING 3

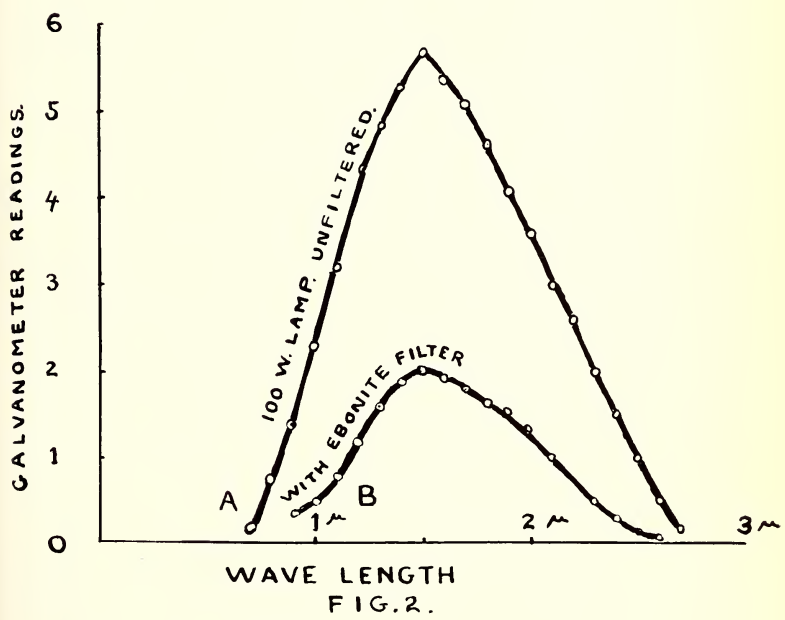
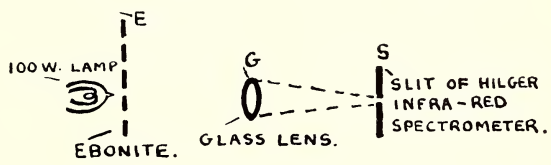
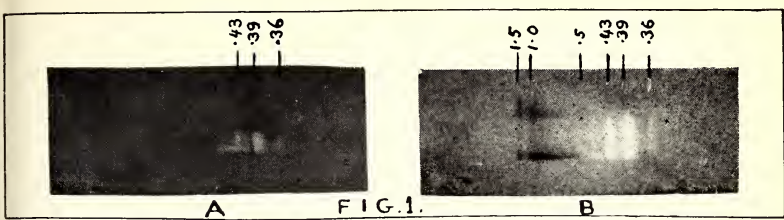
* ZnS-Cu SCREEN ENERGIZED BY 6V LAMP AT SETTING 1



METHOD OF LOCATING POSITION OF THE NEUTRAL POINT.



W & W' ARE ORDINARY PHOTOGRAPHS OF COMB C FIG. 2. THE CENTRAL PART OF EACH HAS BEEN CUT AWAY TO FORM A SLOT, THROUGH WHICH PHOTOS. D & E ARE OBSERVED. ARROWS INDICATE THE PLACE WHERE QUENCHING COMMENCES.



latter are finally plotted against time; see the decay curve, Pl. VIII, Fig. 3.

The photo-electric cell employed is one devised by the author.⁵ It consists of two short lengths of copper wire, carefully cleaned and then oxidized in a Bunsen gas flame; both are immersed in a glass tube filled with ethyl alcohol. One wire is covered with a jacket of porous light-proof paper, and the other is exposed to the light emerging from the slit. The two leads from this cell are connected to a galvanometer. A switch is provided by means of which they can be short-circuited between each reading. See the inset on the top left-hand side of Pl. VIII, Fig. 2, which figure also shows the response curve and other characteristics of this cell.

It has been pointed out by Le Bon⁶ that the two ends of the spectrum have opposite effects upon a ∇ Zn S screen. They come to a balance somewhere in the blue end of green. Exposure to light on the blue side of this and on into the ultra-violet gives an increase of luminosity, whereas exposure to yellow, red, or infra-red causes a quenching of the phosphorescence. Working with a lamp run at a constant voltage, J. C. Maby (at Oxford) has informed the author that he succeeded in making a filter, light transmitted through which had no apparent effect upon Zn S-Cu, and he also demonstrated that a slight increase of either the red or of the blue component of his filter upset the balance, and allowed some of either the quenching or of the energizing radiation to come into action.

SHIFT OF NEUTRAL POINT BETWEEN ENERGIZING AND QUENCHING RADIATIONS.

At the commencement of this paper reference is made to the author's "shift of spectral distribution effect".¹

The following is an experiment designed by the author to show how the neutral point between energization and quenching shifts with varying conditions. A diagram "Z" is given at the upper right-hand side of Pl. IX, which illustrates the arrangement employed. "R" is a resistance in series with a 6-volt metal filament (motor

⁵This cell is fully described in *The Journal of Scientific Instruments* (in the press), and in its earliest form it was described by the author in his paper "Radiometric Condensers and Inductances," *Journal Royal Society of Arts* (London), Vol. LXXXII, Dec. 22, 1933.

⁶"The Evolution of Forces," by Gustave Le Bon. Kegan, Paul, Trench, Trübner and Co., London, 1908.

headlight) lamp, within a metal housing "H", which is open at top and bottom. As indicated, it is provided with a "slit" through which the light from the lamp "L" falls on to a Zn S-Cu (or any other phosphor) screen. "C" is an ordinary comb (with its teeth pointing downwards). The light reaches the screen between the teeth of the comb, space by space as the lamp-house with its lamp and slit is drawn slowly and steadily across from right to left. This movement is achieved by means of a heavy plunger which sinks slowly into a tightly fitting and well-oiled sheath. The speed of travel is regulated by means of an air inlet tap (not shown in the diagram). When the lamp travels across the screen, a sliding contact "S" attached to the underside of the lamphouse also travels across the resistance "R", so that as the lamp moves the current in its circuit is gradually reduced. The comb photographs A to E, Pl. IX, are prints from panchromatic plates. Contact phosphorographs were first made on to the latter direct from the Zn S screen shown behind the comb in the diagram.

A. A \odot screen was placed behind the comb and the 6-volt lamp (unfiltered) was made to travel across it; this caused the screen to fluoresce with diminishing intensity from right to left, where it was exposed to the light from the lamp between the teeth of the comb.

B. In this case the Zn S-Cu screen was first energized by exposure to a 5-ampere d.c. arc between steel electrodes. A black glass filter was placed between the 6-volt travelling lamp and the slit, so that the screen was irradiated by infra-red only. The spaces between the teeth in this photograph appear as black instead of as white lines. The luminosity of the screen was quenched in diminishing degree from right to left.

C. The conditions are similar to those for B, except that in this case the light from the travelling lamp was unfiltered. The result is similar, a gradually diminishing quenching.

D. In this instance the Zn S-Cu screen was energized (as indicated on the diagram "at setting 3") by exposure to the 6-volt lamp, whilst the latter was stationary at position "3", i.e. only a quarter of the resistance was in series with the lamp. The screen thus energized was placed in position behind the comb, and the lamp and sliding contact were then caused to travel across, starting from position "4", i.e. with the lamp taking its full current.

Examination of this phosphorograph D will show that the brightness of the screen was increased at first until "neutral point" was reached (i.e. the position at which the screen was unaffected), and after that the screen was quenched.

E. This is similar to D, except that the screen was energized at a stationary setting "1", i.e. with three-quarters of the resistance in series with the lamp. It will be observed that in this case the "neutral point" has been displaced towards the right. As it was rather difficult to locate the exact position of the "neutral point" on these photographs, the following method was devised.

Method of Locating the "Neutral Point".

A \odot Zn S-Cu screen was placed behind the comb. The series resistance "R" was short-circuited and the 6-volt lamp was made to travel at its full brilliance across the comb. This resulted in a phosphorescing picture upon the screen on which all the spaces between the teeth showed up equally. A contact print was made from this on to photographic paper. A strip was cut out from the centre of this print so as to form a slot extending across the whole length of the picture of the comb.

Two such slotted prints were then placed in position as shown on Pl. IX, D¹ and E¹, over copies of photographs D and E. The latter can be viewed through the slots.

It will be observed that the vertical white lines at the right-hand end of each slotted photograph fit on to white lines on photographs D and E as seen through the slots, but to the left the white lines on the slotted photograph coincide with black lines in the photographs under the slots. The exact point at which the change-over takes place, i.e. the "neutral point", is found quite easily in this way; its position is surprisingly sharply defined. In order to facilitate location the ends of certain teeth of the comb have been removed. Another use to which this apparatus could be put would be to differentiate between the different phosphors, each of which shows a different displacement of neutral point.

PHOSPHOROGRAPHS OF SPARKS.

The author has employed glass-backed Zn S-Cu screens in lieu of photographic plates for taking positive and

negative photographs of sparks.⁷ Instead of sparking on to the film side of a photographic plate placed upon an "earthed" sheet of metal, he sparked on to the zinc sulphide surface of a screen from which he afterwards made phosphorographs. The results were similar to ordinary "spark photographs". No new features of any particular interest were revealed.

As phosphor screens were being employed so often in place of photographic plates in the course of these investigations, it was felt that a comparison would be useful. The following experiment was therefore designed and carried out.

REFLECTION OF INFRA-RED RADIATIONS COMPARISON TESTS BETWEEN ZINC SULPHIDE SCREENS AND PHOTOGRAPHIC PLATES.

Pl. VIII, Fig. 5, shows the general set up. Five small squares of paper—black, white, blue, yellow and red—were attached in that sequence to the face of a "tilt board" C. D is a hollow base box or "runner" in which the baseboard C is able to slide longitudinally. In this way each square can be placed in its turn opposite to a slot T on the upper side of the "runner" D.

A photographic plate (or alternatively a Zn S screen) is fastened to the baseboard by adhesive plaster. The upper side of the runner D screens the plate from all stray light. Radiations from the lamp L are projected by means of a lens (see Fig. 5, A and B) on to one coloured square of paper at a time, and are reflected therefrom so that they pass through the slot T on to the photographic plate (or screen) P. When a screen was employed the exposure required was about twenty-five seconds, and it was only necessary to switch the lamp on and off; but when panchromatic plates were used a simple pendulum shutter was employed in order to give equal exposures of one twenty-fifth of a second.

Pl. VIII, Fig. 6, A, B, C, D, E and F, shows the results obtained. It will be seen that a \odot Zn S screen B gives proportionately the same response to each colour (though

⁷ "Method of Obtaining Static Electricity from an Induction Coil," *Archives of Radiology and Electrotherapy*, 1919, 23, 271-281. An account of the early history of "spark photography" which dates back to 1888 is given in this paper, with references to the work of J. Brown, Lord Armstrong, Campbell Swinton, F. H. Glew, A. W. Rodman, A. W. Porter, C. W. Raffety, M. Toepler, and G. G. Blake.

of course a longer exposure is required) as that of an ordinary standard Kodak plate A. Reflected infra-red radiations from white, blue, yellow and red surfaces quenched a ✕ Zn S-Cu screen (C, Fig. 6) equally, but no appreciable reflection was registered from the black square.

D shows the effect of blue light when reflected on to a ⊙ Zn S-Cu screen.

E shows the quenching caused by rays projected through a red glass filter and reflected on to a ✕ Zn S-Cu screen.

F shows the effect of the same radiations (through a red glass filter) upon a panchromatic plate.

ACKNOWLEDGMENTS.

The whole of the foregoing work has been carried out in the physics laboratories at the University of Sydney, and the author wishes to thank Professor Vonwiller, the authorities and the staff for all the facilities which they have so courteously offered to him, also Mr. N. R. Hansen for his help in making the spectrometric measurements.

FINAL PART OF VOL. LXXIII
ISSUED APRIL 12, 1940

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PART IV

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OF
NEW SOUTH WALES
FOR
1939
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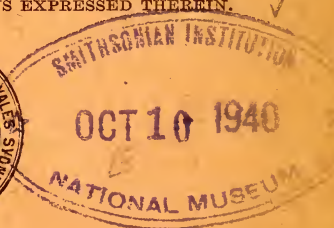
PART IV (pp. 206 to 262 and pp. i to xlviii)

OF
VOL. LXXIII

Containing Papers read in December,
with Plates XI-XVII, also List of Members,
Abstract of Proceedings and Index

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CORRIGENDA.

- P. 208.—Footnote 3: *For* Wade, A., *read* Wade, R. T.
- P. 209.—Line 13: *For* Pl. XI, *read* Pl. VI.
„ Line 15: *For* Pl. XI, *read* Pl. VI.
- P. 210.—Last line: *For* Pl. XI, *read* Pl. VI.
- P. 211.—Line 2: *For* Pl. XI, *read* Pl. VI.
- P. 212.—Line 2 from bottom: *For* Pl. XI, *read* Pl. V.
„ Last line: *For* MF.178 (Pl. XI, Fig. 1), MF.182 (Pl. XI, Fig. 1), *read* MF.178 (Pl. VIII, Fig. 1), MF.182 (Pl. VI, Fig. 1).
- P. 213.—Line 1: *For* Pl. XI, *read* Pl. V.
„ Line 2: *For* Pl. XI, *read* Pl. V.
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„ Line 8: *For* Pl. XI, *read* Pl. V.
„ Line 12: *For* F.110334, *read* F.11033A.
- P. 215.—Line 8: *For* Pl. XI, *read* Pl. VI.
„ Line 24: *For* Pl. XI, *read* Pl. VI.
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VOLUME LXXIII

PART IV

THE TRIASSIC FISHES OF GOSFORD,
NEW SOUTH WALES.

By R. T. WADE, M.A., Ph.D.

(Communicated by DR. C. ANDERSON.)

(With Plate XI and six text-figures.)

(Manuscript received, November 21, 1939. Read, December 4, 1939.)

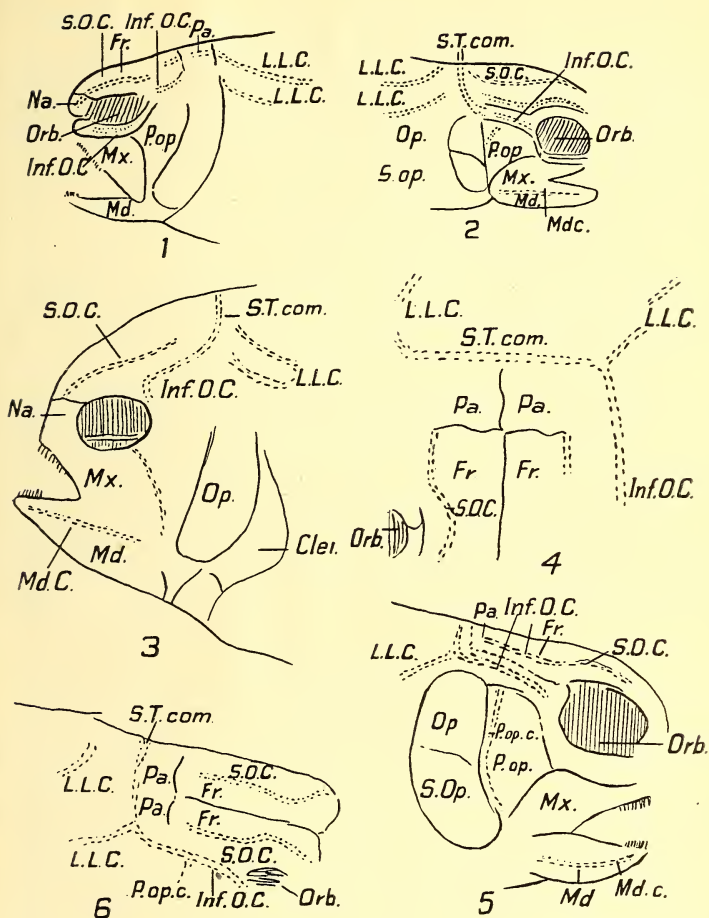
INTRODUCTION.

By the courtesy of the Curator of the Mining and Geological Museum and the Director of the Australian Museum, Sydney, I have been able to examine the collection of fossil fishes which formed the subject of "Memoirs of the Geological Survey of New South Wales, Palæontology, No. 4".¹ The author of that Memoir, Sir Arthur Smith Woodward, assigned the Gosford fishes to ten genera; this paper is concerned with five of these, knowledge of which has increased since 1890, when the Memoir was published. The genera in question are those to which the names *Dictyopyge*, *Peltopleurus*, *Pholidophorus*, *Pristisomus* and *Semionotus* were assigned in the Memoir.

LETTERING USED IN TEXT-FIGURES.

Ang. .. Angular.	Op. .. Operculum.
Ant. orb. Antorbital.	Orb. .. Orbit.
Art. .. Articular.	Pa. .. Parietal.
Clei. .. Cleithrum.	Pal. .. Palatine.
Fr. .. Frontal.	Pas. .. Parasphenoid.
Inf. O.C. Suborbital sensory canal.	P. Mx. Premaxilla.
L.L.C. .. Lateral line canal.	P. op. .. Pre-operculum.
Md. .. Mandible.	P. op. c. Pre-opercular canal.
Md. C. .. Mandibular canal.	S.T. com. Supra-temporal commissure.
Mx. .. Maxilla.	S.O.C. .. Supra-orbital canal.
Na. .. Nasal.	S. op. .. Suboperculum.

¹ Woodward, A. S., "The Fossil Fishes of the Hawkesbury Series at Gosford", *Mem. Geol. Surv. N. S. Wales*, Palæontology, No. 4, 1890.



Figs. 1-6.

Fig. 1.—*Tripelta dubia*; composite, based on MF. 189b.

Fig. 2.—*Chrotichthys gregarius*; composite, based on MF. 858.

Fig. 3.—*Pristisomus gracilis*, head; composite, MF. 864.

Fig. 4.—*Pristisomus gracilis*, roof of skull (378 in the Mining Museum).

Fig. 5.—*Zeuchthiscus australis*; composite, based on MF. 862.

Fig. 6.—*Zeuchthiscus australis*, roof of skull; MF. 861.

Family CATOPTERIDÆ.

Genus *Dictyopyge*.

There is nothing to add to Smith Woodward's description of these fossils; the material is too poorly preserved and it is impossible to determine the osteology of the head. But for that reason the writer thinks that reference to the genus *Dictyopyge* cannot be upheld. *Dictyopyge* is now known (Brough²) to have a peculiar skull roof, a nearly vertical suspensorium and a nearly homocercal tail; not only are the bones of the head of the Gosford Catopteridæ unknown, but the suspensorium approaches the vertical only in *D. symmetrica*, and the tail is hemiheterocercal, having a scaly lobe at least half as long as the whole tail.

On the other hand, the species named "*D. illustrans*" and "*D. robusta*" resemble *Helichthys* Broom and *Brookvalia* Wade³ in the obliquity of the suspensorium, the proportions of the trunk, the squamation, the shoulder girdle, the length of the fleshy lobe of the tail, and the ornamentation, and it is possible that they are species of *Brookvalia*. "*D. symmetrica*", which has a differently shaped head and nearly vertical suspensorium, possibly represents another genus.

Family PERLEIDIDÆ.

Genus *Tripelta*,⁴ nom. nov.

Diagnosis. Small Perleididæ with slightly deepened trunks, large orbits placed anteriorly and well above the oral margin, and blunt snouts. Gape wide; suspensorium nearly vertical. Frontals and nasals large; operculum and suboperculum in one deep quadrangular plate; preoperculum quadrangular. Maxilla triangular, deepest just behind orbit; mandible weak and tapering. Paired fins small, pelvics closer to anal than to pectoral arch. Origin of dorsal fin just anterior to that of anal. Median fins equal in size. Tail with very short fleshy upper lobe. Fin rays distally branched, divided into segments of moderate size, proximal segment the longest; fulcra not preserved.

² Brough, J.: On Fossil Fishes from the Karroo System, etc., *Proc. Zool. Soc. Lond.*, 1931, Pt. I, 235.

³ Wade, A.: The Triassic Fishes of Brookvale, New South Wales, British Museum (Nat. Hist.), 1935.

⁴ From Gr. *pelte*, light shield, referring to the three rows of deepened anterior flank scales.

Scales smooth, several rows on anterior flank greatly deepened.

Genotype. *Peltopleurus dubius* Smith Woodward.

Remarks. Distinctive features of the genus are the comparatively wide gape in association with a nearly vertical suspensorium, the delicate mandible, and the squamation.

Tripelta dubia (Smith Woodward).

(Pl. XI, Fig. 1; Text-fig. 1.)

Diagnosis. As for genus.

Holotype. The impression of a nearly complete fish in the Australian Museum on a slab numbered MF. 189 B, the original of Pl. XI, Fig. 4.¹

Material. The holotype and three other specimens in the same collection, namely MF. 187 (Pl. XI, Fig. 5¹), MF. 860, F. 6464.

Description. The dimensions of the holotype are as follows: total length to base of caudal pedicle, 5.2 cm.; maximum depth of trunk, 1.9 cm.; length of head with opercular apparatus, 1.3 cm. The length of the fish is nearly three times the depth of the trunk, and is four times the length of the head.

The head is short, with a blunt snout. The orbits are moderately large, and placed well above the oral margin. The gape is rather wide, the suspensorium nearly vertical. The sutures between the bones of the cranial roof are not preserved, but some sections of the sensory canal system have left deep impressions, and it cannot be doubted that the nasals and frontals were large, the parietals and tabulars short, the circumorbitals and temporals shallow.

No line of division could be found in the deep, short, opercular plate, which includes the operculum. The upper margin of the preoperculum is not determinable, but it is clearly large, quadrangular, with an acute-angled projection between the suboperculum and the maxilla, and placed nearly vertically. The maxilla, which articulates rigidly with the preoperculum, is triangular, having its base the oral margin and its greatest depth at a point below the back of the orbit. The mandible is weak and tapering.

The paired fins, of which the pelvics are closer to the anal fin than to the pectoral arch, are small and badly preserved. The dorsal, anal and caudal fins each comprise about twelve rays, and the origin of the dorsal fin is just anterior to that

of the anal. The fin rays branch distally and are divided into segments of moderate length except proximally, where the segments are long. No fulcra are preserved. The upper lobe of the tail is very short.

The smooth scales are arranged in about twenty-eight transverse rows, reckoning from the pectoral arch to the first caudal fin ray, and there are no more than eight or ten scales in an anterior row. The principal scales of the anterior flank are deep, for example 4.5 mm. \times 1.6 mm.

Genus *Chrotichthys*⁵ nom. nov.

Diagnosis. Small Perleididæ with slender bodies, blunt snouts and large orbits placed anteriorly. Gape moderate, suspensorium nearly vertical. Skull bones faintly ornamented. Operculum slightly deeper than suboperculum; preoperculum large, quadrangular. Maxilla large, triangular; mandible stout, deep posteriorly, slightly tapering towards the front. Teeth minute, sharply pointed.

Paired fins small; pelvics equidistant from anal and pectoral arch. Origin of dorsal fin just in front of that of anal. Fin rays well spaced. Tail with short upper lobe.

Scales smooth, margins entire, greatly deepened on anterior flank.

Genotype. *Pholidophorus gregarius* Smith Woodward.

Remarks. The structure of the jaws is of itself sufficient to preclude reference of this form to the genus *Pholidophorus*. Distinctive characteristics are the slender proportions, the rather small mouth, the comparatively shallow and proportionately long opercular apparatus, the deep flank scales, and the spacing of the fin rays.

Since the type specimen and several others have been lost it is necessary to select as lectotype the counterpart of the type.

Chrotichthys gregarius (Smith Woodward).

(Pl. XI, Fig. 2; Text-fig. 2.)

Diagnosis. As for genus.

Lectotype. An incomplete fish, MF. 858, in the Australian Museum, the counterpart of the type, which is figured by Smith Woodward (Pl. XI, Fig. 6).¹

⁵ Name derived from Gr. *Chros* (*chrotos*), dark coloured, referring to the mode of preservation.

Material. The lectotype and two other specimens, MF. 858 (on same slab as lectotype) and MF. 859 (Pl. XI, Fig. 10).¹

Description. These small fishes have been badly crushed and no specimen is complete. The measurements of the lectotype are as follows: length from tip of snout to origin of anal fin, 2.8 cm.; maximum depth of trunk, 0.75 cm.; length of head with opercular apparatus, 0.7 cm.

One of the specimens (MF. 858) measures 3.2 cm. from the back of the operculum to the base of the tail, and has a maximum depth of 1.1 cm. Hence, if 1 cm. be allowed as the length of the head of this specimen, the length of the fish is approximately four times the maximum depth.

The thin closely fitting bones of most of the head have left only faint impressions, but the slightly thicker bones of the cranial shield have been pressed upwards and display the supra-orbital sensory canals and the transverse commissures on both sides of the mid-line of the head. The operculum and suboperculum of nearly equal depth form a single quadrangular plate, the length of which is rather great compared with its depth. Their common suture, as uncertainly revealed in specimen MF. 858, is slightly sinuous and oblique, and occurs a little below the middle line of the total opercular covering, so that the operculum must be deeper than the suboperculum. The line of junction of maxilla and preoperculum is faintly revealed in specimen MF. 859, running from the lower end of the suboperculum to the lower corner of the orbit. Preoperculum and maxilla are thus seen to be large plates rigidly articulating and completely covering the cheek. In the upper part of the preoperculum there is a branch of the sensory canal, which leaves the infraorbital branch slightly in front of the operculum and passes backwards and downwards.

The mandible, stout and deeply channelled by a branch of the sensory canal system, is deepest at the angle of the mouth, tapering slightly anteriorly. The gape is moderate, the suspensorium nearly vertical. The paired fins are very small, the pelvics, which are situated half way between the anal fin and the pectoral arch, comprising only about six short rays. In the median fins the rays are well spaced, but they are poorly preserved, and it is impossible to say whether they branch distally, are divided into segments, or bear fulcra. The origin of the dorsal fin, which includes about thirteen rays, is just anterior to that of the anal,

which has more than ten rays. The caudal fin is incompletely known, sixteen rays being preserved.

The scales, which are moderately thick and have left smooth impressions, were arranged in about thirty transverse rows, of which an anterior row includes about ten scales. Anterior scales of the lateral line are about twice as deep as long.

Genus *Pristisomus* Smith Woodward.

Diagnosis. Small Perleiidæ with moderately deep fusiform bodies, short heads and orbits of moderate size anteriorly placed. Suspensorium nearly vertical; gape small. Operculum and suboperculum, about equal in area, in one deep quadrangular plate. Mandible deepest at angle of mouth, tapering anteriorly. Teeth long and peg-like. Paired fins small, pectorals long, pelvics closer to anal fin than to pectoral arch. Median fins remote; origin of dorsal slightly anterior to that of anal. Fin rays well spaced, divided to the base into short segments; branched distally. Fulcra present. Upper lobe of tail very short, caudal fin scarcely forked. Scales smooth; several rows of scales very deep.

Genotype. *Pristisomus gracilis* Smith Woodward.

Remarks. Distinctive characteristics of the genus are the small head, the shape of the head, the depth and shape of the trunk, the remote position of the fins and their division to the base into short segments, the very small upper lobe of the tail and the considerable depth of several rows of flank scales.

The genus was held to include three species, exhibiting slight difference in proportions, in the number of rays in the dorsal fin, and in the relative depth of the flank scales. But the variation in the proportions of the typical members of the three species is no greater than that shown by individuals assigned to any species, and the number of fin rays and the sizes of the scales are in all cases only approximately determinable. Therefore, since the head, too, is incompletely known, it seems unnecessary to recognize more than one species, *P. gracilis*. Variations may be attributed to differences in maturity, or to differences in the manner in which individuals have been crushed.

The following are the specimen numbers of the individuals as assigned by Smith Woodward¹ to the three species respectively: *Pristisomus gracilis*: MF. 177 (Pl. XI, Fig. 1), MF. 178 (Pl. XI, Fig. 1), MF. 182 (Pl. XI, Fig. 1), MF. 863,

MF. 864, MF. 865, F. 38906-7. *P. latus* : MF. 181 (Pl. XI, Fig. 3), MF. 186 (Pl. XI, Fig. 4), MF. 866. *P. crassus* : MF. 179 (Pl. XI, Fig. 7), MF. 867, MF. 189 A.

Pristisomus gracilis Smith Woodward.

(Pl. XI, Fig. 3 ; Text-figs. 3, 4.)

Diagnosis. As for genus.

Holotype. An imperfect fish in the Australian Museum numbered MF. 177 (the original of Pl. XI, Fig. 1).¹

Material. The holotype and fifteen other specimens in the same collection, namely MF. 178, MF. 179, MF. 181, MF. 182, MF. 186, MF. 189A, MF. 863, MF. 864, MF. 865, MF. 866, MF. 867, F. 6463, F. 110334, F. 38906-7 ; three specimens in the Mining Museum, 157, 378, and 386 ; and numerous unregistered fragments.

Description. The measurements of the holotype are as follows : total length to base of caudal pedicle, 9.5 cm. approximately ; maximum depth of trunk, 4.1 cm. The head is incomplete anteriorly. The average total length of seven fishes is 9.8 cm., and their average maximum depth 4.4 cm. Hence the length is about two and a quarter times the depth. The average length of the head, including the opercular apparatus in four specimens the trunks of which have a maximum depth of 4 cm. is 2.4 cm. Since the bones of the head were thin, and closely adjusted, sutures are not well preserved. The sensory canal system, however, is well revealed. The mid-line of the head descends very rapidly from a point above the back of the orbits to the oral margin, which it meets almost at right angles. The eye is small, placed anteriorly, and well above the oral margin. The suspensorium must be nearly vertical but the gape is small. The structure of the cranial roof is not precisely known, but from the positions of the well preserved sensory canals it is clear that it was of normal Perleidid character, with large nasals and frontals, short tabulars, and shallow temporals and circumorbitals.

The suture between maxilla and preoperculum appears faintly in one specimen only, but there is no doubt that the cheek was covered mainly by a large maxilla and a large preoperculum rigidly articulating. Operculum and suboperculum form a single quadrangular plate, much deeper than long, and divided—if specimen MF. 178 is correctly interpreted—at about half its length. The lower jaw,

deepest at the angle of the mouth, is slender anteriorly. Rows of long peg-like teeth are well preserved on the jaws.

The walls of the sensory canal are completely broken, and no tubuli are preserved, but the canals have left deep impressions, filled in many instances with a white mineral. The supraorbital branches pass from quadrangular nasals into the frontals, curve concentrically above the orbit, and end far back on the head, close to the transverse commissure, from which the infraorbital branch curves forwards parallel to the mid-line of the head, sweeping down in a graceful curve at a short distance from the orbit—the conditions indicating narrow tabulars and temporals. From the infraorbital canal, the preopercular branch is directed downwards and backwards for a short distance. Of the shoulder girdle only the cleithrum is revealed in part. It is deep and only moderately long.

The paired fins, of which the pelvics are nearer to the anal fin than to the pectoral arch, are small, comprising only about half a dozen rays each.

The dorsal fin, the origin of which is only a short distance anterior to that of the anal fin, is made up of about sixteen rays, as is the anal fin. The rays are distally branched and divided to the base into small segments. Strong fulcra are present. The tail has a very short upper lobe, and the caudal fin, which comprises about twenty-two rays, is scarcely cleft.

The scales, which are apparently smooth and have entire margins, are arranged in about thirty-two transverse rows, an anterior row including about fifteen scales. The principal flank scales are much deeper than long, for example, 5 mm. \times 2 mm.

Genus *Zeuchthiscus*⁶ nom. nov.

Diagnosis. Small Perleididæ which have slightly deepened fusiform bodies, short heads, and large orbits anteriorly placed. Gape small, suspensorium slightly inclined forwards. Frontals large, constricted between the orbits and slightly widened behind them. Operculum quadrangular, short, placed nearly vertically. Maxilla triangular, large, deepest behind orbit. Mandible short, tapering. Teeth long and peg-like. Paired fins small; pelvics closer than to pectoral arch. Origin of dorsal in advance of that of anal. Fin rays well spaced, divided

⁶ Name from Gr. *Zeuchthe*, he is imprisoned.

into numerous segments, of which the proximal are longest ; distally branched. Fulcræ well developed. Tail with very short upper lobe. Caudal fin scarcely forked. Scales apparently smooth, deeper than long on anterior flanks.

Genotype. *Semionotus australis* Smith Woodward.

Remarks. The name " *Semionotus australis* " was tentatively assigned to " a single imperfect specimen wanting the head and anterior part of the trunk " (Pl. XI, Fig. 2).¹ There are, however, in the collection other specimens from which a more complete description can be compiled, and from which it is perfectly clear that, while the structure of cheek and jaws shows that the genus may not be placed in the Semionotidæ, all the known characters are those of typical Perleididæ.

The smaller individuals called *tenuis* have, in this paper, been included in the type species because they differ from the larger only in being slightly more slender, as is not unusual in the juvenile members of a species.

Zeuchthiscus australis (Smith Woodward).

(Pl. XI, Fig. 4 ; Text-figs. 5, 6.)

Diagnosis. As for genus.

Holotype. An imperfect specimen, lacking the head and fore part of the trunk, in the Australian Museum, numbered MF. 188 (Pl. XI, Fig. 2).¹

Material. The holotype and five other specimens, namely MF. 861 (a nearly perfect fish), MF. 862 (head and part of the trunk) and MF. 183 (*Semionotus tenuis* of Smith Woodward)¹ in the Australian Museum ; two less mature individuals on slab No. 386 in the Mining Museum, named thereon *Semionotus tenuis* (Pl. XI, Fig. 3).¹

Description. The measurements of specimen MF. 861 are as follows : total length to base of caudal pedicle, 16·5 cm. ; maximum depth of trunk, 6·2 cm. ; length of head with opercular apparatus, 3·5 cm. Thus the length is nearly two and two-thirds times the maximum depth of the trunk, which is a little less than twice the length of the head. The two smaller specimens are a little more slender and have proportionately larger heads.

Although the suspensorium is nearly vertical, the gape is small. The orbits are large and anteriorly situated, and the snout is blunt.

The heads are badly crushed and sutures are not well preserved, but the sensory canals have left deep impressions,

filled throughout much of their length with a white mineral. Nearly the whole cranial roof is covered by a pair of large frontals, the common suture of which is slightly sinuous, and which are deeply channelled by the supraorbital branches of the sensory system. These end posteriorly at the slightly sinuous sutures of the frontals with the parietals, which are small and probably nearly square. The limits of the tabulars are not known with certainty. Anteriorly the sensory canals pass into large quadrangular nasals, but the snouts are so badly crushed that delimitation of the bones of that region is impossible.

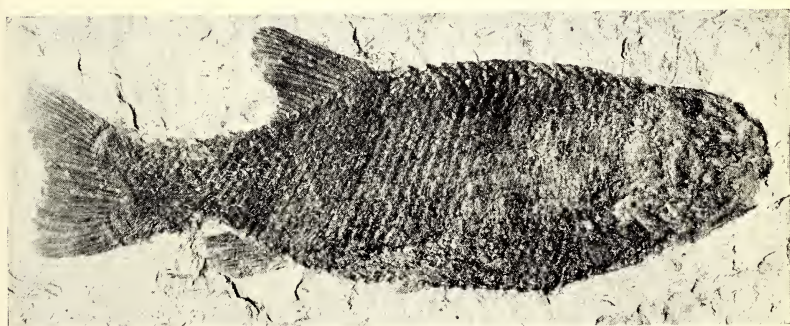
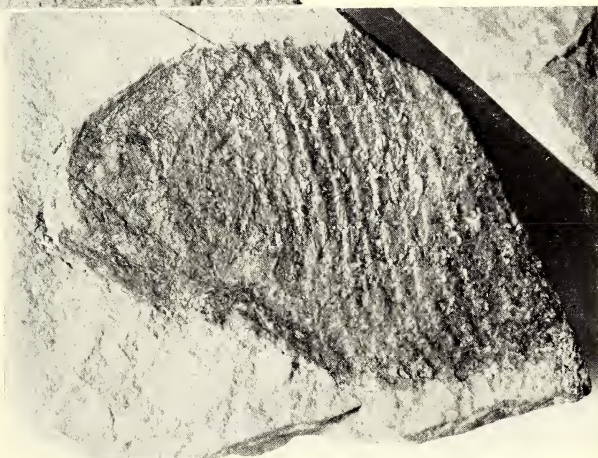
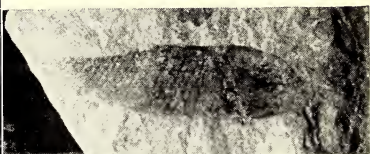
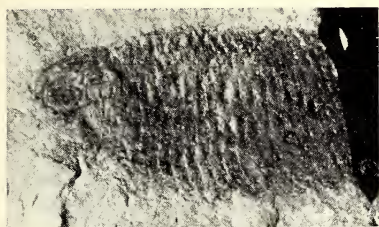
The opercular shield is deep and short and includes two plates only, which are of nearly equal depth—the operculum, quadrangular and the suboperculum, triangular and a little deeper than the operculum, which it meets in a slightly sinuous line of junction.

The preoperculum, which is firmly fixed to, and rigidly articulating with, the maxilla, is very deep and short and placed nearly vertically on the cheek. Inferiorly it is wedged between the suboperculum and the maxilla, its common suture with which runs from the lower corner of the suboperculum to the postero-inferior corner of the orbit. The maxilla is large, roughly triangular, and is deepest at about half its length, becoming very shallow below the orbit. The mandible is rounded posteriorly, deepest below the angle of the mouth, and tapered anteriorly. The teeth are long and peg-like.

The pectoral fins are not preserved, but the small pelvic fins, which are placed a little nearer to the anal fin than to the pectoral arch, include about six or eight rays.

The fin rays of the median fins are divided into segments, of which the proximal segments are long; distally they are unknown. Fulcræ are present. The dorsal fin, including eighteen to twenty rays, is completely in advance of the anal fin, which includes about twelve. The tail has a very short fleshy upper lobe and the caudal fin of about twenty-six rays is scarcely cleft.

The scales are smooth, with entire margins, and the principal flank scales are much deeper than long, being smaller and more nearly equilateral dorsally, ventrally and posteriorly. They are arranged in about forty transverse rows, an anterior row containing probably sixteen scales.



CONCLUSION.

The classification of the Gosford fishes is as follows :

Selachii : Genus non-det.

Dipnoi : *Gosfordia truncata*.

Palæoniscidæ : *Myriolepis clarkei*, *M. latus*, *Apateleopis australis*.

Catopteridæ : Genus non. det. (two species). Genus non. det. (one species).

Perleididæ : *Chrotichthys gregarius*, *Pristisomus gracilis*, *Tripelta dubius*, *Zeuchthiscus australis*.

Belonorhynchidæ : *Belonorhynchus gigas*, *B. elegans*.

Cleithrolepidæ : *Cleithrolepis granulata*, *C. lata*.

This association indicates a horizon not higher than the base of the Middle Trias.

ACKNOWLEDGMENT.

The author gratefully acknowledges the encouragement and help of Prof. D. M. S. Watson.

EXPLANATION OF PLATE XI.

Fig. 1.—*Tripelta dubia*, MF. 860.

Fig. 2.—*Chrotichthys gregarius*, MF. 858.

Fig. 3.—*Pristisomus gracilis*, MF. 864.

Fig. 4.—*Zeuchthiscus australis*, MF. 861.

Figs. 1-3 slightly greater than natural size ; photographed by G. C. Clutton.

Fig. 4, about one-half natural size ; photographed by H. Gooch.

THE EFFECT OF ŒSTROGENS ON THE POUCH OF THE MARSUPIAL TRICHOSURUS VULPECULA.

By ADOLPH BOLLIGER, Ph.D.,
and ARTHUR CARRODUS, M.B., M.S.

(With Plates XII-XIV.)

(Manuscript received, November 22, 1939. Read, December 6, 1939.)

THE DEVELOPMENT OF THE POUCH.

There is already a considerable literature on the development of the pouch of marsupials, which in general also covers the development of the pouch of *Trichosurus vulpecula*. According to Bresslau (1912), who examined *Didelphys marsupialis*, the pouch is formed by epidermal thickenings or down growths which appear on either side of the mammary area and which connect posteriorly, thus enclosing the mammary area caudally. Then these epithelial plates become solid ridges and later delamination appears in the lateral limbs, separating them into dorsal portions which are continuous with the mammary area, and ventral portions which are reflected medially and thus form a recess. This recess is the beginning of the pouch proper, which is due to infolding, and the ridges become the future lips of the pouch.

In *Trichosurus vulpecula* (silver-grey or long-eared possum) after about two weeks of extra-uterine life the future pouch can be demonstrated macroscopically, consisting of two lateral ridges joining posteriorly at about an angle of 45° and enclosing a groove containing the mammary area. The delineation soon becomes more marked, and as further growth takes place the edge of the mammary area carries the inner limb of the ridge along with it, forming a recess. This recess, representing the interior of the pouch, increases in size approximately at the same rate as the mammary area develops, and in the pouch embryo of about four months of age the recess is about 1 mm. in depth at the posterior end where the two ridges or lips join together.

During the next few months the lips rearrange themselves approximately in parallel planes, leaving a narrow linear furrow between them which represents the opening of the pouch. At the age of about ten months this opening is about 2 to 3 cm. in length, and the interior of the pouch is represented by an approximately circular recess, which opens cephalad and is of about 0.5 cm. in depth at the posterior end of the pouch. Approximately at the caudal end of the opening of the pouch are found two small nipples of about 1 mm. in length on either side of the pouch recess, while the mammary glands are not palpable at this stage. The lining of the pouch is clean and covered with a small amount of soft white hair.

Usually with the advent of a breeding season, namely either around the months of March or August, a comparatively sudden increase in the size of the pouch may be noted, which up till then grew at about the same rate as the animal itself. Within a few days the depth of the pouch proper as measured from the posterior margin of the opening to the caudal end of the pouch cavity increases from 0.5-2 cm. to 3-4 cm., and a corresponding increase is also noted in the lateral recesses, while the lips remain comparatively stationary. The mammary glands become palpable plaques of about 1 cm. in diameter and the nipples increase somewhat in size. At the same time the pouch is found to be moist, and this is partly due to the secretion of an oily fluid which varies in colour from a light orange to a deep rich orange-brown. When freshly secreted, this fluid seems to be practically colourless or pale orange but turns orange-brown when exposed to air. These observations point to a state of œstrus which, particularly in autumn (March and April), may be followed by pregnancy. If no pregnancy occurs the secretion of the oily coloured substance diminishes or stops, while the fluid dries up and ultimately becomes deposited as dark brown flakes. The pouch itself diminishes in size, but does not attain pre-œstrous dimensions. If pregnancy occurs, the period of uterine gestation is short as observed in many other marsupials. Amongst our laboratory animals, in one instance birth was found to occur sixteen days after mating. This, however, may not be the actual gestation period, because the male was left with the female for several days.

The pouch enlarges still further during the time (five months) in which the young is reared in this organ and

ultimately a female of about 2·2 kg. body weight is capable of housing a young of about 0·4 kg. body weight. Soon, however, the mother is unable to accommodate in its pouch the rapidly growing young, but as observed in our animals kept in captivity it may allow the offspring to suck one of its nipples, which by now may have reached a length of 1·3 cm. In order to accomplish this without the necessity of the young entering the pouch it forms by means of the lips of the pouch, a sphincter-like round opening of about 0·5-1 cm. in diameter through which the elongated nipple protrudes and becomes accessible to the offspring. At this stage the pouch begins to regress in size and, after the young ceases to suck, the mammary gland and nipple also regress. But the pouch always remains somewhat larger than it was before the first pregnancy, and after repeated pregnancies the pouch never seems to be less than 2-3 cm. in depth. Later, the animal comes into œstrus again, and the pouch increases in size to become ready for the next pregnancy (Pl. XII).

ANATOMICAL FEATURES OF THE POUCH MUSCULATURE.

The muscles connected with the pouch consist of the panniculus carnosus and the "sphincter marsupii". The panniculus carnosus of *Trichosurus vulpecula* is well developed as in other marsupials. The pars pudenda of this muscle consists of fibres which are found in the skin covering the caudal part of the ventral aspect of this animal. In the immature possum it consists of comparatively few fibres, which run roughly in the antero-posterior direction over the entire lower abdomen. However, in the lips of the pouch these muscle fibres are found to be present in such large numbers as to form two distinct bundles, which decussate at the posterior end of the pouch and then split into two wide thin bands, which decussate with the muscle fibres which run in the antero-posterior direction, and together with them ultimately enclose the cloacal region. Cephalically these bundles leave the lips of the pouch anteriorly and then converge into one strand, which for some distance runs parallel with the mid-line and then becomes attached as muscle to the linea alba for a distance of about 2-3 cm. From the appearance of these muscle bundles, one seems justified in differentiating between the fibres forming the pudental part of the panniculus carnosus in general and the fibres found in the lips of the pouch which have been called in the past "sphincter marsupii",

although a recent worker on the American marsupials considers this differentiation superfluous (Enders, 1937). In *Trichosurus vulpecula*, this "sphincter marsupii" forms an elongated sling, which ultimately is attached to the upper part of the linea alba and whose main function seems to be to close the pouch opening.

On the other hand, the fibres of the panniculus carnosus, as distinct from the "sphincter marsupii", seem to play an important rôle in support of the pouch wall when a pouch embryo is present. However, as pointed out, it is but little developed in the sexually immature animal, but on approaching the first period of œstrus these fibres undergo hypertrophy and hyperplasia as shown by the gross appearance and by microscopic examination. On placing one's finger inside the pouch during this period, one notices a distinct compressing action of the panniculus carnosus which is different from the sphincter-like action of the "sphincter marsupii", which has also undergone hypertrophy. With a growing young in the pouch this organ and its muscles become extended. After the young has left the pouch, this cavity regresses in size, but the pouch muscles remain more pronounced than they were before pregnancy, and after further pregnancies they may reach a thickness of 2-3 mm. near the lips (Pl. XIV, Fig. 1).

In connection with the mammary apparatus the so-called compressor mammæ has to be mentioned. This muscle corresponds to the cremaster muscle in males. It is likewise derived from the transversus abdominis and internal oblique muscles and crosses the inguinal area, terminating in the mammary gland. On microscopic examination this muscle is seen divided into numerous fibres between the lobules of the mammary gland. During pregnancy it was found to undergo hypertrophy. On the other hand, the tissue lining the interior of the pouch is very thin and contains only a few muscle fibres, but it contains numerous fine tortuous blood vessels permitting elongation of the vessels as the pouch is expanded.

EXPERIMENTAL.

In contrast to a previous investigation which dealt mainly with pigment formation in young possums (Bolliger and Carrodus, 1938) emphasis is now laid on changes observed in possums which had borne young and which consequently possessed well developed pouches which measured from 2-6 cm. in depth. This variation in depth

depended on whether the animal was in œstrus or had had young recently or not. Eight such females were injected weekly with œstrone, œstrodol benzoate, or œstrodol dipropionate in dosages ranging from 5,000 to 50,000 international units or 0.5 mg. to 5 mg. However, in spite of the greatly varying dosage and different types of œstrogens administered the results were of a uniform nature with regard to changes in and around the pouch so that they can be described together.

One to three days after the first injection the lips of the pouch were found to be thickened and the nipples were turgid and glistening. The interior of the pouch became moist, mostly due to the secretion of an orange coloured oily substance. In a few more days the whole pouch became turgid and the coloured secretion increased in amount and stained the hairs in and around the pouch with a deep orange or brown colour. This secretion when freshly removed from the pouch with the finger had a pale orange colour which darkened to an orange brown when exposed to the air. During the week following a second injection the lips of the pouch became more swollen and the pouch cavity distinctly smaller. After three to six weekly injections, depending somewhat on the dosage, the pouches which originally measured from 2.6 cm. in depth and 3.5 cm. in width became shallow recesses of only about 0.5 cm. in depth or less. The lips of the pouch were found to be swollen and puckered and in a state of tonic contraction. The rest of the pouch was also typically in a state of contraction and the nipples were rigid and firm but their size was not altered much, while the mammæ became distinctly smaller. As a result of the contraction of the pouch the nipples moved cephalad and became situated under the lips of the contracted pouch (Pl. XIII).

In this group of animals further observations were impossible because they invariably died from urinary obstruction and general toxæmia resulting from a swelling of the median vagina which was secondary to epithelial proliferation, keratinisation, and infection. This aspect of œstrogenic activity, however, will be discussed on another occasion. On histological examination, the pouches of these animals showed marked muscular hyperplasia (Pl. XIV). In immature possums, where the panniculus carnosus is always thin, this muscle was found to be at least twice as thick in treated animals as in controls. At the same time œdema was observed between many

of the bundles of muscle fibres and between the actual fibres themselves. Some isolated fibres stained faintly as if undergoing necrosis. The vessels in the pouch musculature were dilated. Similar changes were observed in the muscle bundles found in the mammary glands (endings of compressor mammæ).

In some animals where only one large injection of œstrodiol benzoate or œstrodiol dipropionate was given, the pouch underwent identical changes but the animals survived. For example, a female with a pouch of 3 cm. in depth was injected with 0.8 mg. of œstrodiol dipropionate (Ovocycline, Ciba). Next day the margins of the pouch opening were found to be thickened and in the next few days it definitely decreased in size. Ten days after the injection the depth of the pouch was only 0.5 cm. or less, and the ridges of the pouch were swollen and puckered and the whole of the pouch area seemed to be in a state of tonic contraction. This state remained for another ten days and then the pouch increased again in size and had nearly reached its pre-experimental dimensions about one month after the injection. However, the lips as well as the ventral covering of the pouch appeared to be thicker than they were pre-experimentally.

In a previous communication (Bolliger and Carrodus, 1938) the effect of small doses of œstrogens on immature females has been demonstrated. It has been shown that in sexually mature females a single injection of 900 units of "œstroform" brings on the production of pigments and thickening of the margin of the pouch as well as an increase in the size of the pouch. However, it had been overlooked that small doses of œstrogens (e.g. 200 international units) give a definite reaction in possums which had borne young. After such an injection it was observed that a secretion of fresh pigment occurred and that the margin of the pouch became thicker. The pouch also appeared to increase somewhat in size about a fortnight after the injection.

With regard to the pigment as observed in the pouch, it must be pointed out that in all probability a similar pigment is secreted in the urine of males as well as females. The freshly voided urine is light yellow in colour, but when left standing for several days until it turns alkaline it takes on a brownish red colour, which on further standing returns to a dark brown. In fresh urines the addition of ammonia hastens the appearance of the brownish red colour, which may become visible a few hours after the addition of

ammonia. So far the chemical nature of this urinary pigment as well as that from the pouch remain unknown, but being produced by the same animal and being of a similar colour they may be related to each other. So far, however, no relationship could be established between the urinary secretion of the pigment and the administration of oestrogens, because the pigment was observed in the urine of treated and untreated animals and no attempt has been made yet to measure the amounts secreted.

DISCUSSION.

Trichosurus vulpecula, a marsupial commonly found in N. S. Wales, has a well developed pouch which shows marked reactions towards the administration of oestrogens. After the injection of small doses of oestrogen (200 to 1,000 units) development of the pouch and mammary glands becomes evident, particularly in sexually immature animals. Furthermore, hyperplasia of the pouch muscles is noted as well as the secretion of a pigment which is deposited within the pouch and which stains the hairs within the pouch as well as those around it. After the administration of one or several moderate doses of oestrogen (1,000 to 10,000 units) hyperplasia and hypertrophy of the muscles of the pouch (as demonstrated microscopically) occur and the pouch decreases in size. After the administration of a single large dose of oestrogen (50,000 to 100,000 units) the hypertrophy and hyperplasia of the pouch muscle become very marked and it goes into a state of contraction which is accompanied by an almost complete disappearance of the pre-experimental pouch. If the injections of oestrogens are maintained the contraction of the pouch remains permanent, but the animal dies from the action of the hormone on the internal reproductive organs.

This end result is similar in animals which possess small or large pouches pre-experimentally, but it naturally becomes much more obvious in animals which had large pouches before injecting the oestrogen, i.e. females which had had several pregnancies and which were in a state of oestrus.

This reaction indicates that the muscle of the pouch (which is voluntary muscle) is contracted by oestrogens. This is somewhat analogous to the recently reported action of oestrogens on the cremaster of *Trichosurus vulpecula* (Bolliger and Carrodus, 1939) and it is quite probable that

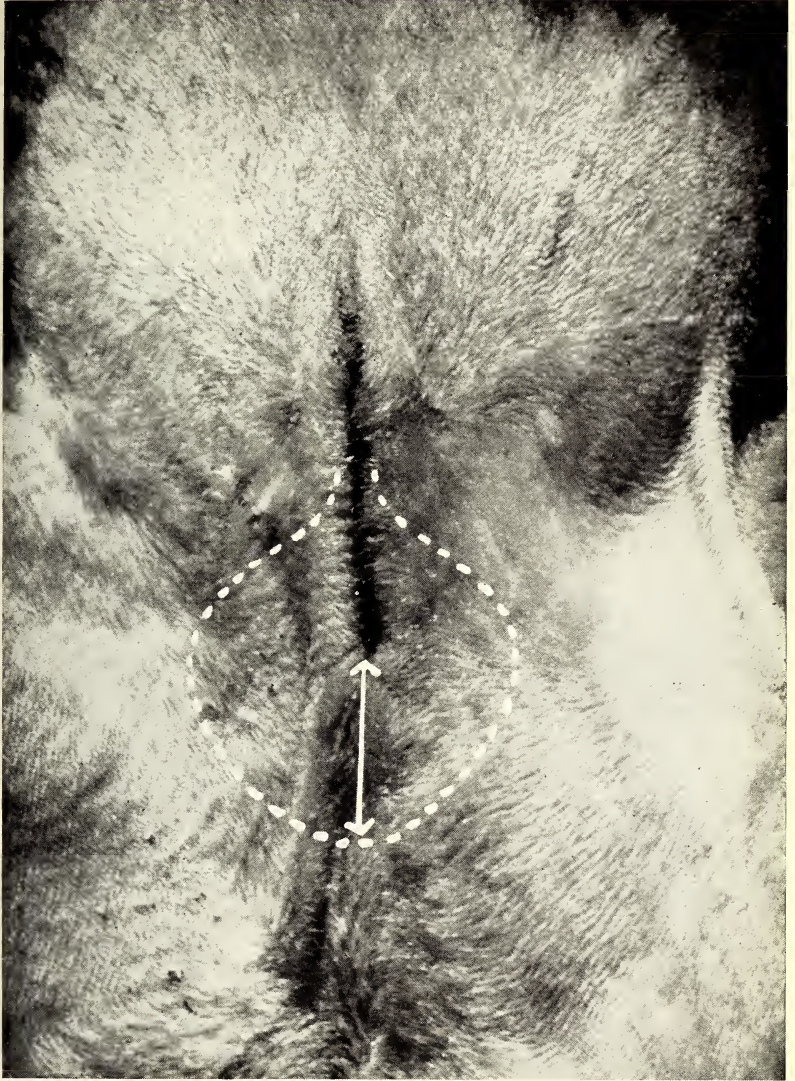






Fig. 1.



Fig. 2.



Fig. 3.

in the present experiments the compressor mammæ which corresponds to the cremaster muscle in the male is, to some extent, responsible for the "ascent" of the mammary glands which takes place when the pouch contracts. However, the action of the compressor mammæ would be less marked, since it is a smaller muscle than the cremaster.

While appreciating the fact that uterine musculature is an entirely different structure, nevertheless comparisons may be drawn between the reactions of the voluntary muscles of the pouch and the involuntary muscles of the uterus of higher mammals to injections of œstrogens. In the latter case, contractions are also produced, which, however, last only for a short time, while the contractions produced in the pouch of our marsupial are of long duration and even permanent if the injections are maintained. Furthermore, after the administration of œstrogens the myometrium of higher mammals shows hyperplasia, hypertrophy, and necrosis (Zondek, 1936), as observed in the muscle of the pouch of *Trichosurus vulpecula*.

The secretion of the orange brown pigment after the administration of œstrogens has already been referred to in a previous communication (Bolliger and Carrodus, 1938) and a relationship between gonadal activity and pigment formation in the pouch has been postulated. This has been confirmed in the present investigation and secretion of pigment after the administration of œstrogens could be demonstrated in pouch young as soon as they became covered with hair as well as in all the females. It is, however, more pronounced in almost fully grown females than in pouch young, and it is most marked in sexually mature animals, where the oily substance is secreted in such quantities as to become deposited as thick brown flakes over the whole fundus of the pouch after desiccation. No progress has been made in the study of the chemical nature of the pigment secreted in the pouch, but it was found that a pigment of apparently similar nature is habitually secreted in the urine, in treated as well as untreated females and males.

Finally, it may be pointed out that these observations on the pouch of *Trichosurus vulpecula* can be made to a large extent on the intact animal, while on the other hand observations on the myometrium of higher mammals either necessitate killing large numbers or severe operative interference.

SUMMARY.

The administration of large doses of œstrogen to *Trichosurus vulpecula* brings on a contraction of the pouch, which is accompanied by, and probably due to, the contraction of the pouch muscle. Other reactions observed are hypertrophy of the pouch muscle and secretion of pigment within the pouch, effects which are also obtained with smaller doses.

ACKNOWLEDGMENTS.

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EXPLANATION OF PLATES.

PLATE XII.

Lips of pouch of *Trichosurus vulpecula* which had borne young. The dotted line indicates the approximate demarcation of the pouch cavity. The arrow indicates the "depth" of the pouch.

PLATE XIII.

Pouch of *Trichosurus vulpecula* after the administration of large amounts of œstrogen (250,000 international units) administered over a period of five weeks. The small contracted pouch is forcibly everted to show the turgid nipples and deposit of pigment. Note size of pouch and lips in relation to finger-nails. The pre-experimental length of the lips was 3.5 cm. and the depth of the pouch was 2.5 cm.

PLATE XIV.

Fig. 1.—Microphotograph of strip of skin taken from an area corresponding roughly to that indicated by the arrow in Pl. XII. This specimen was obtained from an untreated possum which had a small young in its pouch. The panniculus carnosus is of moderate thickness. $\times 6$.

Fig. 2.—Cross section through pouch of fully grown possum which had been treated with large doses of oestrodiol dipropionate (15 mg. administered over a period of two weeks). The section shows the remaining small pouch cavity (the pre-experimental pouch was approximately 4.0 cm. in width at this level), the redundant thickened skin lining the pouch, and the thickened pouch muscle. Part of a mammary gland can be seen below the pouch cavity. $\times 6$.

Fig. 3.—Microphotograph of a strip of tissue removed from an area corresponding roughly to that indicated by the arrow in Pl. XII. This specimen was obtained from a possum which had been treated with repeated injections of oestrone (13 mg. administered over a period of seven weeks). The section indicates the thickening of the pouch muscle, particularly in the region of the sphincter marsupii. $\times 6$.

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THE ACTION OF PROGESTERONE ON THE POUCH
OF THE MARSUPIAL TRICHOSURUS VULPECULA.By ADOLPH BOLLIGER, Ph.D.,
and ARTHUR CARRODUS, M.B., M.S.

(With Plates XV-XVII.)

(Manuscript received, November 21, 1939. Read, December 6, 1939.)

The essential actions of progesterone are concerned with important uterine functions during the menstrual cycle and pregnancy. During the menstrual cycle it transforms the endometrium from the proliferative to the secretory or progestational phase and during pregnancy it maintains the endometrium in a condition necessary for the maintenance of pregnancy and it inhibits uterine motility.

The administration of progesterone to a marsupial (*Trichosurus vulpecula* or common possum) with a well developed pouch has brought on changes in the pouch and the mammary apparatus which indicate certain functions of this hormone which have not yet been recognised.

EXPERIMENTAL.

Since the development and the anatomy of the normal pouch of *Trichosurus vulpecula* have been reviewed in another paper (Bolliger and Carrodus, *THIS JOURNAL*, 1939, 73, 218), an account of only the experimental changes will be given on this occasion, and observations which were made on a pouch young and two fully grown females will now be described.

Experiment 1. The pouch young was about three months old and still in the hairless stage when the experiment was started (Pl. XV). It received weekly injections of 2 mg. of synthetic progesterone (Lutocycline, Ciba) over the whole period of observation, namely five months, and was compared with an uninjected control and with pouch embryos of about similar age which were injected with other sex hormones such as testosterone propionate and oestrodioldipropionate. The findings in the female injected with progesterone were typical and were as follows. The

mammary glands, which were not visible before injections were started, became evident within one week. The nipples also increased in size and the lips of the future pouch were more raised than in uninjected controls. After four weekly injections the lips of the future pouch were represented by two swollen ridges of 2-3 mm. in height, and the mammary glands were about 3-4 mm. in diameter and filled up nearly the whole area between the lips, while in the uninjected control they were still hardly visible at this stage. The nipples were also enlarged and were capped with an orange-brown secretion.

For another five or six weeks the mammæ remained large and even increased in size. Then the mammæ and nipples became smaller and the ridges of the pouch became less raised, although the injections were continued. Three months after beginning the injections, the ridges forming the lips of the future pouch had retrogressed and the mammary glands had practically disappeared, while the nipples had diminished to the size of a pin's head. Five months after beginning the injections, a pouch, in the proper sense of the word, had not yet formed, because no cavity was present as in controls of similar age and the lips met posteriorly at an angle of about 90° instead of being approximately in parallel planes. Near the point where they met, the ridges were comparatively well developed, but no recess was present beneath them and the nipples were in full view. Under stress, the animal succeeded in bringing the lips together, but this was only a temporary expedient, and in the normal relaxed condition the pouch area remained completely open (Pl. XVI), while in the untreated control, as well as in those young females which had been treated with other sex hormones, at this age an actual pouch had been established.

Experiment 2. The next specimen examined was a fully grown but small female which apparently had not yet had young. The pouch was well developed and measured about 2 cm. in depth and 2 cm. in width. The hairs covering the interior of the pouch were stained a deep orange and the lips of the pouch were thin and habitually closed. The mammary glands were about 0.8 cm. in diameter and the nipples 0.2 cm. at their base. An injection of 5 mg. of progesterone was given and during the following week the pouch enlarged slightly. A further injection of 5 mg. was given in the second week and a final injection of 2 mg. in the third week of the experiment.

After the last injection the pouch was found to be definitely smaller, measuring about 0.5 cm. in depth and 1.0 cm. in width, and kept on decreasing in size. After about six weeks following the first injection the pouch had practically disappeared, inasmuch as the lips became reduced to slightly raised ridges which had opened up anteriorly forming an angle of about 45°. This exposed the fundus of the original pouch covered by orange-stained hairs and all the infolded skin had disappeared. The mammary glands were hardly visible and the nipples presented themselves as small structures of the size of a pin's head. This condition simulating an eversion of the pouch remained practically unaltered for five more months, while the mammary glands and the nipples increased somewhat in size.

Experiment 3. The next experiment dealt with an older animal which had a young in its pouch for a period of about three months. Then it lost its young by accident. At this stage the pouch was distended, large and lax. It measured about 5 cm. in depth and 5 cm. in width, and the lips were rather thin and habitually closed. The mammary gland from which the young derived its nourishment was about 2.0 cm. in diameter and its nipple was 1.0 cm. in length.

On 14/9/39, 18/9/39, and 21/9/39 intramuscular injections of synthetic progesterone of 5 mg. each were given.

3/10/39. The pouch had regressed in size. Its depth was now only 1.0 cm.

10/10/39. The depth of the pouch was now only 0.5 cm. The lips were thin, and, instead of being approximated to each other as found in controls, they formed a loose ring through which the deeply brown coloured hairs covering the fundus of the pouch could be seen. But no fresh pigment was formed in the shallow pouch, which was perfectly dry. Nipples and mammary glands had decreased in size. The diameter of the large mammary gland was about 0.8 cm.

13/10/39. Five mg. of progesterone were injected subcutaneously.

20/10/39. The appearance of the pouch was approximately the same as ten days ago. It was very lax and readily turned out. The nipple on which the young was sucking was now 0.3 cm. in length, while the other one was only the size of a pin's head.

26/10/39. Little of the original pouch remained. At the posterior end the depth beneath the lips was about 0.2 cm., while the maximum lateral recesses reached a depth of 0.6 cm. (Pl. XVII). The fundus or floor of the pouch was only slightly wrinkled (see Pl. XVII). Then the animal was killed. On removing the skin from the lower abdomen the muscle in the lips of the pouch (sphincter marsupii) was found to be thin as compared with that of untreated females which had had young after a similar interval of time. The rest of the pouch muscle (panniculus carnosus) was also thin. The compressor mammæ also appeared to be thinner than in controls. With regard to other post-mortem findings it may be of interest to note that all the other organs appeared to be normal and the clitoris was small. It was only 0.2 cm. in length and 0.1 cm. in width.

DISCUSSION.

The primary action of progesterone on the pouch of *Trichosurus vulpecula* is an increase in the size of the pouch and mammary gland development. This reaction is quite evident in sexually immature females and young females with small pouches, while it is less obvious in older animals. This, as well as the secretion of pigment as observed in the sexually immature animal, may be interpreted as an oestrogenic or gynæcogenic action of progesterone. But a few weeks after the administration of fairly large doses of progesterone, involution of the mammary apparatus is observed and regression of the pouch is brought on or hastened by this hormone. This regression may ultimately take on the form of an eversion. It actually seems as if the pouch had a tendency to regress to the stage seen in the hairless pouch embryo of about two to three months of age, when the lips of the future pouch appeared as two divergent ridges which demarcated a "V"- or "U"-shaped area, while the pouch proper had not yet been established. On the other hand a pouch young of about three months of age, injected with progesterone, does not develop a proper pouch in which the lips are approximated such as develops in controls of similar age.

In comparing the action of oestrogens with that of progesterone one finds that they, when given over a short period of time in smaller doses, tend to increase the size of the pouch, and when given in large doses tend to abolish

the pouch. But while in the end progesterone brings on muscular atony and probably atrophy, and tends to convert the pouch into an open area corresponding to the fundus of the original cavity, suggesting a process of eversion, oestrogens bring on muscular hypertrophy and contraction of the pouch.

SUMMARY.

In *Trichosurus vulpecula* progesterone at first appears to bring about mammary gland development and an increase in the size of the pouch. This is followed by a converse effect as the experiment is prolonged, in as much as the mammary glands atrophy. The pouch regresses in size and in some cases undergoes a process of eversion.

ACKNOWLEDGMENT.

The authors are indebted to Mr. T. M. Harkness of Ciba Ltd. for presenting the progesterone (Lutocycline) used in this investigation.

DESCRIPTION OF PLATES.

PLATE XV.

Pre-experimental appearance of pouch in the living, hairless, pouched young.

PLATE XVI.

Showing the open pouch area with the nipples in full view four months after beginning the injections of progesterone.

PLATE XVII.

Experiment III. Showing rapid and far-reaching involution of a pouch which one month previously contained a fair-sized young.

For appearance of normal pouch, see THIS JOURNAL, 1939, 73, Pl. XII (Bolliger and Carrodus).

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MAGNETIC STUDIES OF COORDINATION
COMPOUNDS.PART I. COBALTOUS COMPOUNDS—WITH SPECIAL
REFERENCE TO THEIR RESOLVABILITY.By D. P. MELLOR, M.Sc.,
and R. J. GOLDACRE, B.Sc.

(Manuscript received, November 22, 1939. Read, December 6, 1939.)

As judged by the magnetic criterion for bond type, octahedral complexes of Co^{III} are, with rare exceptions, essentially covalent structures. A very comprehensive study of cobaltic amines made by R. Rosenbohm (*Zeit. für. physikal Chem.*, 1919, 93, 693) revealed that complexes containing NH_3 , H_2O , OH^- , $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$ are diamagnetic, a fact which has since been interpreted (L. Pauling, *Jour. Amer. Chem. Soc.*, 1931, 53, 1367) as showing that the bonds to the Co^{III} are covalent in character. While magnetic data are available for only a few of the many octahedral Co^{III} complexes which have been resolved into optically active antipodes, in each instance the complex has proved to be diamagnetic and hence an essentially covalent structure. This is true for $[\text{Co}(\text{en})_3]^{+++}$ and $[\text{Co}(\text{C}_2\text{O}_4)_3]^{=}$ * and it is almost certain to be true for all the other complexes which have been resolved since they involve similar bonds to cobalt. In the course of a recent discussion on the stereochemistry of complex oxalates C. H. Johnson (*Trans. Farad. Soc.*, 1932, 28, 845) has pointed out that while it has proved possible to resolve the essentially covalent complex $[\text{Co}(\text{C}_2\text{O}_4)_3]^{=}$ all attempts to resolve $\text{K}_3[\text{Fe}(\text{C}_2\text{O}_4)_3]$ and $\text{K}_3[\text{Mn}(\text{C}_2\text{O}_4)_3]$ † have failed. These last two substances are paramagnetic, with moments corresponding to those expected for essentially ionic complexes. It is a matter of some interest to inquire how far this correlation between covalent character and

* Unpublished data for $[\text{Co}\{\text{Co}(\text{en})_2(\text{OH})_2\}(\text{NO}_3)_6]$ indicate that cobalt atoms in this complex contain no unpaired electron spins.

† Attempts to resolve mangani salicylates have also failed (G. J. Burrows, private communication).

resolvability extends. Magnetic data will not always serve to distinguish between ionic and covalent complexes even of the transition elements; for example, ionic and covalent complexes of copper and chromium are indistinguishable magnetically. The distinction can, however, be drawn in the case of Fe^{II} and it is significant that the only octahedral ferrous complex resolved, namely $[\text{Fe}(\text{dipy})_3]^{++}$ (dipy=dipyridyl) (A. Werner, *Berichte*, 1912, 45, 433) is diamagnetic (L. A. Welo, *Phil. Mag.*, 1928 (7), 6, 481) and hence an essentially covalent complex. As far as the magnetic evidence goes, few essentially covalent complexes of Fe^{III} , Mn^{II} or Mn^{III} have been described. The only ones appear to be the complex cyanides of these metals. At the same time none of these metals has been resolved in the valency states indicated.

Since resolutions of either tetrahedral or octahedral complexes of Co^{II} have not been reported, the magnetic investigation of a number of cobaltous compounds was undertaken. A table showing predicted moments of complexes containing transition elements has been drawn up by L. Pauling and M. L. Huggins (*Zeit. für. Krist.*, 1934, 87, 714). For covalent complexes of Co^{II} , either square or octahedral, a moment equal to 1.73 Bohr magnetons, corresponding to the existence of one unpaired electron is expected; for ionic complexes, on the other hand, a moment of 3.88 Bohr magnetons,* corresponding to the existence of three unpaired electrons, is expected. From Tables I and II it can be seen that all the complexes examined are ionic in character, that is the bonds $\text{Co}^{\text{II}}-\text{N}$ and $\text{Co}^{\text{II}}-\text{O}$ are of the ion dipole type.

That cobaltous compounds have not been resolved may well be due, at least in part, to the fact that any complexes which have been investigated have been ionic in character; in any case attempts to resolve complexes of this type under varying conditions are perhaps worth while, if only to test further the significance and limitations of the correlation between resolvability and bond character.

While there is a good deal of evidence to show that the chances of effecting a resolution are probably very much greater in the case of essentially covalent complexes, it is not possible to say, on the basis of existing data, just how much ionic character of the metal—non-metal bonds

* Moments larger than this are generally found, the larger values being attributed to the added effect of orbital contribution.

renders resolution difficult or impossible. There are reasons for believing that other factors than the ionic or covalent nature of the complex may enter into the question of its resolvability, always assuming of course that the proper limitations of symmetry obtain.

Resolutions have indeed been reported for complexes which on grounds other than magnetic are believed to possess considerable ionic character. By using the relation connecting bond character with the difference in electronegativity of the atoms linked together it can be shown that Al-O and Be-O bonds should each possess about 60 per cent. ionic character (L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, New York, 1939, p. 70).

Nevertheless claims to have resolved complexes involving tetrahedral metal oxygen bonds have been made in regard to (i) salts of beryllio-benzoylpyruvic acid (W. H. Mills and Gott, *Jour. Chem. Soc.*, 1926, 31, 21); (ii) salts of aluminooxalic acid (G. J. Burrows and K. H. Lauder, *Jour. Amer. Chem. Soc.*, 1931, 53, 3601; Wahl, *Berichte*, 1927, 60, 399). In regard to salts of aluminooxalic acid it should be pointed out that C. H. Johnson (*Trans. Farad. Soc.*, 1932, 28, 845) states that working with aqueous solutions he failed to effect a resolution of aluminooxalic acid.

Burrows and Lauder on the other hand carried out the actual resolution—the separation of the strychnine d and l salts—in *non-aqueous media*. This is a point of considerable significance because in such media ionisation of the complex is much reduced. It seems to indicate that, while ionic complexes apparently cannot be resolved in ionising media, they should not necessarily be regarded as non-resolvable on that ground alone. Magnetic evidence should therefore be useful in suggesting a technique likely to be successful in resolution work on cobaltous complexes.

EXPERIMENTAL.

Susceptibility measurements were made by the Gouy method with an electromagnet producing a field of approximately 6,000 gauss for a current of 5 amps. Calibrations were made with chemically pure $\text{NiSO}_4(\text{NH}_4)_2\text{SO}_4\cdot 6\text{H}_2\text{O}$, $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ and $\text{FeSO}_4(\text{NH}_4)_2\text{SO}_4\cdot 6\text{H}_2\text{O}$. Weighings were made with an Oertling balance, the sensitivity of which was 1.2 divisions per mgm.

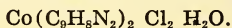
MATERIALS USED.

Hexammine Cobaltous Chloride.

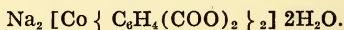
This substance was prepared by adding molten hydrated cobaltous chloride to 20E ammonia solution. The pinkish-brown crystalline substance formed was rapidly filtered and dried in an atmosphere of ammonia. (Analysis $\text{Co}=25.6\%$. Calculated for $\text{Co}(\text{NH}_3)_6\text{Cl}_2$, $\text{Co}=25.4\%$). Other methods of preparation were tried and several specimens were measured. On standing, the susceptibility of all specimens decreased owing presumably, to the formation of dia-magnetic cobaltic complexes. The mean of the two highest values is considered to be the most reliable measurement, and this only is reported.

Tris Ethylenediamine Cobaltous Chloride.

This substance was prepared by the addition of the calculated quantity of ethylenediamine hydrate (dissolved in absolute alcohol) to an absolute alcoholic solution of cobaltous chloride. The pinkish-yellow crystalline solid which separated was filtered and dried as rapidly as possible. It was about as unstable as the hexammine salt, slowly darkening on standing and at the same time becoming less paramagnetic. For this reason it is probable that the susceptibility reported (the highest value measured), although that theoretically required for three unpaired electrons, is still too low owing to partial oxidation to a diamagnetic cobaltic complex.

Cobaltous bis 8-amino-quinoline Chloride.

This compound has been described by G. J. Burrows and E. Ritchie (*THIS JOURNAL*, 1938, 72, 113). We are indebted to these authors who very kindly placed at our disposal this compound and the one referred to in the following section.

Sodium Cobaltophthalate.

For the description of this compound see *THIS JOURNAL*, 1938, 72, 178.

Table I summarises the experimental results obtained in the present investigation. Table II contains data for cobaltous complexes obtained by other investigators.

TABLE I.

Substance.	Molar Susceptibility $\chi_M \times 10^{-6}$.	Magnetic Moment μ (in Bohr Magnetons).
$\text{Co}(\text{NH}_3)_6\text{Cl}_2$	10,382	4.96
$[\text{Co}(\text{en})_3]\text{Cl}_2$	6,225	3.82
$\text{Co}(\text{C}_9\text{H}_8\text{N}_2)_2\text{Cl}_2\text{H}_2\text{O}$	9,687	4.79
$\text{Na}_2[\text{Co}\{\text{C}_6\text{H}_4(\text{COO})_2\}_2]\text{H}_2\text{O}$	11,860	5.35
$(\text{NH}_4)_2\text{Co}(\text{CNS})_4\text{H}_2\text{O}$	7,303	4.16

TABLE II.

$[\text{CoCl}_2(\text{NH}_3)_2]\alpha^1$	12,750	5.50
$[\text{CoCl}_2(\text{NH}_3)_2]\beta^1$	12,400	5.41
$[\text{CoBr}_2(\text{NH}_3)]\alpha^1$	13,100	5.56
$[\text{CoBr}_2(\text{NH}_3)]\beta^1$	12,200	5.38
$[\text{CoI}_2(\text{NH}_3)_2]\alpha^1$	8,900	4.56
$[\text{CoI}_2(\text{NH}_3)_2]\beta^1$	8,850	4.56
$\text{Co}(\text{N}_2\text{H}_4)_2\text{Cl}_2$	—	4.93
$\text{Co}\{\text{CH}(\text{COCH}_3)_2\}_2^3$	7,882	4.18–4.34
CoPy_2Cl_2 violet ²	—	5.34
CoPy_2Cl_2 blue ²	—	4.60

¹ W. Klemm and Schüth, *Zeit. für anorg. allg. Chem.*, 1933, 210, 33.

² E. P. Barkworth and S. Sugden, *Nature*, 1937, 139, 374. Unpublished measurements by N. Faull agree with these values.

³ Int. Critical Tables, Vol. VI, 358. Since the temperature at which this measurement was made was not stated, moments have been calculated for 0° C. and 20° C. respectively.

All moments were calculated after the molecular susceptibility had been corrected for diamagnetic contribution, and on the assumption of the validity of Curie's law for these complexes.

DISCUSSION.

From the results of Table I it may be inferred that there is a fairly general tendency for Co^{II} to form electrostatic

(ion dipole) bonds in contradistinction to the almost universal tendency of Co^{III} to form covalent bonds. In cobaltic complexes $\text{Co}^{\text{III}}-\text{O}^*$ and $\text{Co}^{\text{III}}-\text{N}$ bonds are covalent, while in cobaltous complexes $\text{Co}^{\text{II}}-\text{O}$ and $\text{Co}^{\text{II}}-\text{N}^{2\dagger}$ bonds are essentially ionic.† This difference in the nature of cobaltous and cobaltic complexes is naturally reflected in their chemical behaviour.

Whereas $[\text{Co}^{\text{III}}(\text{NH}_3)_6]\text{Cl}_3$ is quite a stable compound and does not display any reversible decomposition pressure of ammonia below that at which complete and irreversible decomposition takes place, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ readily loses ammonia, particularly when moist. On being shaken up with water $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$ is readily hydrolysed to a blue insoluble basic salt with the loss of ammonia. The behaviour of the ionic complex $[\text{Co}^{\text{II}}(\text{NH}_3)_6]^{++}$ towards water is in striking contrast to that of the covalent complex $[\text{Co}^{\text{II}}(\text{CN})_6]^-$ which readily reduces water with the liberation of hydrogen. The difference of 0.6 Å. between the bond lengths $\text{Co}^{\text{III}}-\text{N}$ and $\text{Co}^{\text{II}}-\text{N}$ discussed by J. S. Anderson (*Aust. Chem. Inst. Journ. and Proc.*, 1939, 6, 235) is improbably large. Accepting the octahedral radius of Co^{III} as 1.22 Å. (L. Pauling and M. L. Huggins, *Zeit. für Krist.*, 1934, 87, 205), the length of the link $\text{Co}^{\text{III}}-\text{N}$ should be approximately 1.92 Å. Very widely different values have been reported for the parameter u of $[\text{Co}(\text{NH}_3)_6]\text{I}_3$ (P. P. Ewald and C. Hermann, *Strukturberichte*, 1913-28, 1, 457); R. Wyckoff, $u=0.20$; H. Hentschel and F. Rinne, $0.15 < u < 0.175$; K. Meisel and W. Tiedje, $u=0.175$. The last value which appears to be the most reliably determined, leads to a value of 1.9 Å.U. for $\text{Co}^{\text{III}}-\text{N}$, in reasonable agreement with the expected value.

Turning next to $[\text{Co}(\text{NH}_3)_6]\text{Cl}_2$, which has the K_2PtCl_6 structure, the first reported parameter $u=0.25$ (P. Stoll, Dissertation, *Räumgitter von Komplexen*, Zurich, 1926) is obviously too large, since it leads to a value of approximately 1.1 Å. for the radius of Co^{++} and a value of approximately 2.6 Å. for the $\text{Co}^{\text{II}}-\text{N}$ bond. By adopting the value of 0.72 Å.U. for the crystal radius of Co^{II} (L. Pauling,

* Except in $\text{Co}_2(\text{SO}_4)_3(\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$.

† Except in $\text{K}_2\text{Ca}[\text{Co}(\text{NO}_2)_6]$.

‡ Co may well form square covalent complexes with atoms less electronegative than nitrogen and oxygen, as for example arsenic and sulphur. Several complexes which probably belong to this class are being investigated.

“The Nature of the Chemical Bond”, *loc. cit.*) and 1.5 Å.U. as the value of the van der Waal radius of nitrogen, the length of the $\text{Co}^{\text{II}}-\text{N}$ bond should be about 2.2 Å.U. The value of 2.12 Å. reported by O. Hassel (*Zeit. für anorg. allg. Chem.*, 1933, 211, 21, also *Strukturberichte*, 3, 475) is in reasonable agreement with the calculated value when one takes into account the uncertainty of 0.1 Å. in the van der Waal radius for nitrogen.

Magnetic data may be used to discuss the constitution of the pairs of substances having the composition $[\text{Co}(\text{NH}_3)_2\text{X}_2]$ (where $\text{X}=\text{Cl}$, Br or I), which have long been regarded as *cis* and *trans* isomers respectively. (Biltz, *Zeit. für anorg. allg. Chem.*, 1914, 89, 128, and F. H. Burstall, *Annual Reports of the Progress of Chemistry*, 1938, 35, 162). From the data of K. Klemm and W. Schüth (*loc. cit.*) it can be seen that the cobalt atom in each of these compounds has three unpaired electrons. Cobalt cannot therefore be square coordinated in these complexes, since this would require one electron to be unpaired. The compounds contain ionic octahedral or tetrahedral complexes similar to those occurring in CoPy_2Cl_2 and MnPy_2Cl_2 (D. P. Mellor and C. D. Coryell, *Journ. Amer. Chem. Soc.*, 1938, 60, 1786). The argument that cobalt is square coordinated in $\text{CoSeO}_4\cdot 5\text{H}_2\text{O}$, because this crystal is apparently isomorphous with $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ (E. G. Cox and W. Wardlaw, *Science Progress*, 1938, 32, 463) is not supported by magnetic data. The moments measured for solid $\text{CoSO}_4\cdot 7\text{H}_2\text{O}$ and cobalt sulphate solution show that water is attached to cobalt by ion dipole bonds. Magnetic measurements have apparently not been made on $\text{CoSeO}_4\cdot 5\text{H}_2\text{O}$, but there is no reason to suppose that the $\text{Co}^{\text{II}}-\text{O}$ bonds are not ionic in this hydrate also.

SUMMARY.

Magnetic susceptibility measurements show that the tendency is for Co^{II} to form essentially ionic octahedral and tetrahedral complexes when groups are attached through nitrogen and/or oxygen atoms.

ACKNOWLEDGMENT.

We are indebted to Professor O. U. Vonwiller, who very kindly provided facilities for carrying out the magnetic measurements in the Physics Department.

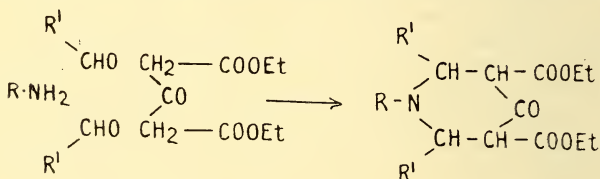
Department of Chemistry,
University of Sydney.

A SYNTHESIS OF OCTAHYDROPIRROCOLINES.

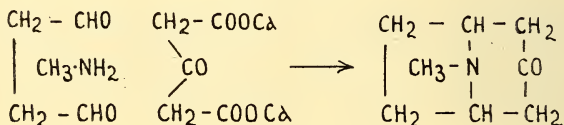
By FRANCIS LIONS, B.Sc., Ph.D.,
and ALAN M. WILLISON, M.Sc.

(Manuscript received, November 22, 1939. Read, December 6, 1939.)

Robinson, in a classical paper (*J.C.S.*, 1917, *111*, 762), described a synthesis of tropinone (I), which involved a reaction very closely related to the general Petrenko-Kritschenko synthesis of γ -piperidones (cf. *Berichte*, 1906, *39*, 1358; 1907, *40*, 2882; 1908, *41*, 1692; 1909, *42*, 2020, 3684, 3693, 3688; *Journ. pr. Chem.*, 1912, *85*, 1; cf. also Mannich, *Arch. Pharm.*, 1934, 272, 323). In essence, this latter consists in the condensation of a primary amine with two molecules of an aldehyde and one molecule of diethyl acetonedicarboxylate, according to the scheme:



The tropinone synthesis involved the variation that both aldehyde groups were parts of the same (succindialdehyde) molecule.

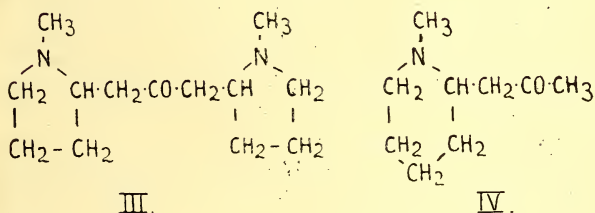
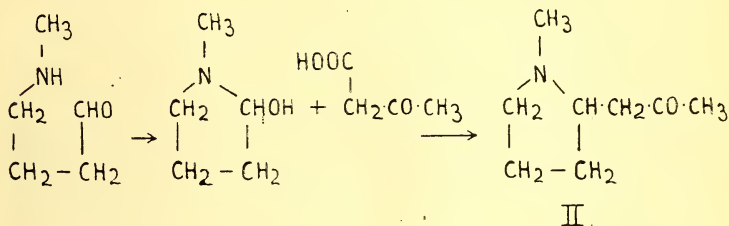


I.

Its success led Robinson (*J.C.S.*, 1917, *111*, 876) to put forward a theory of the phytochemical synthesis of certain alkaloids which has proved to be most fruitful, and, in recent years has been amply elaborated and largely

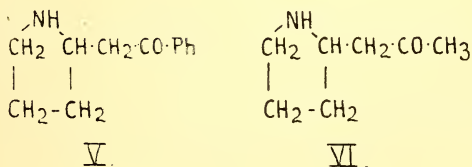
confirmed, mainly by the brilliant researches of Schöpf and his co-workers. (For a review see Schöpf, *Angewandte Chemie*, 1937, 50, 779-87, 797-805; Schöpf and Thierfelder, *Annalen*, 1939, 537, 143-56.)

Robinson and Schöpf, in these discussions of biosynthesis, have suggested that the alkaloids hygrine (II) and cuskhygrine (III) which occur in coca leaves, are probably derived from γ -methylaminobutyraldehyde:

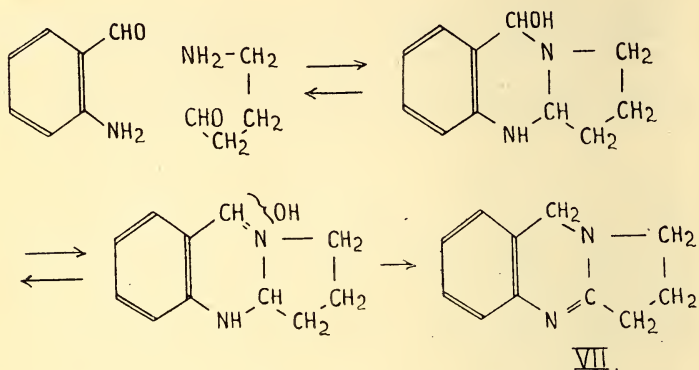


and that methyl isopelletierine (IV), which accompanies ψ -pelletierine, is probably derived in a similar manner to (II) from the homologous δ -methylaminovaleric aldehyde. These aldehydes in turn are to be considered as products derived from ornithine and lysine respectively.

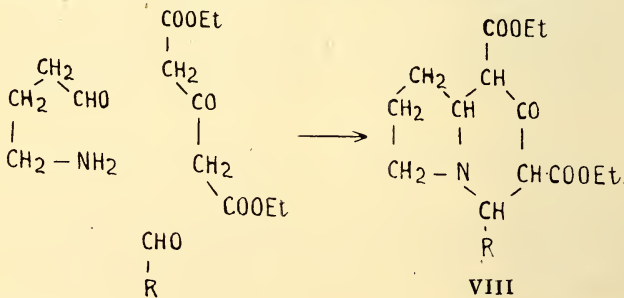
Schöpf was able to show experimentally that γ -amino-butyraldehyde can be condensed with benzoylacetic acid at pH 5 to give the base (V), although he could not obtain nor-hygrine (VI) from the same aldehyde and acetoacetic acid.



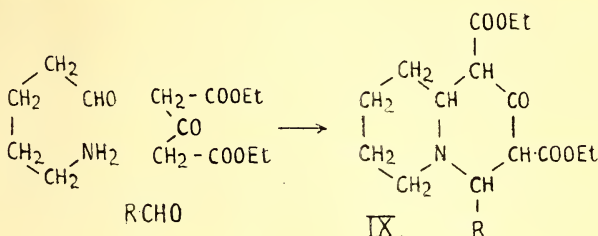
Schöpf, also, has been able to condense *o*-aminobenzaldehyde with γ -aminobutyraldehyde at pH 5 to desoxyvasicine (VII).



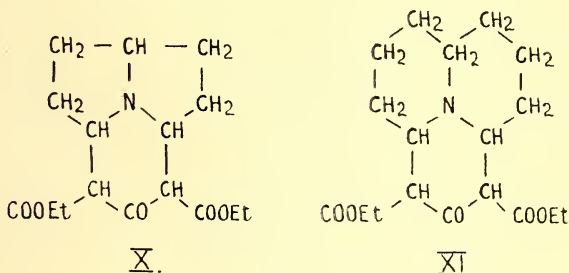
Syntheses of these types make use of the simultaneous presence of two reactive groups in a single molecule to obtain cyclic systems in the final products. Thus, in the tropinone and ψ -pelletierine (cf. Menzies and Robinson, *J.C.S.*, 1924, 125, 2163) syntheses, the two reactive groups (-CHO) are similar, and the final product is bicyclic. In the desoxyvasicine synthesis the groups are dissimilar (-NH₂ and -CHO) and again a bicyclic heterocyclic system results. An obvious extension of the Petrenko-Kritschenko synthesis, therefore, is one in which the primary amino group and one, or even both, of the aldehyde groups are simultaneously present, suitably spaced, in the same molecule. Thus, γ -aminobutyraldehyde should condense, under the right conditions, with acetone dicarboxylic ester in presence of another aldehyde to an octahydropyrrocoline derivative (VIII) according to the scheme :



Similarly, δ -aminovaleric aldehyde should afford a reduced pyridocoline derivative (IX).



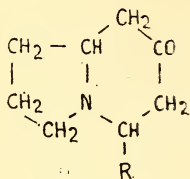
An amino dialdehyde, such as γ -aminopimelic aldehyde, should be capable of condensation with acetone-dicarboxylic ester to yield the pyrrolizidine derivative (X), whilst δ -aminoazelaic aldehyde should give the pyridocoline derivative (XI).



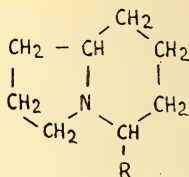
Each of these bases should have a most interesting stereochemical configuration.

The experiments described in the present paper show that it is possible readily to produce bases of type (VIII) in yields as high as 95% of theory, by combining together an aldehyde (1 mol.), diethyl acetonedicarboxylate (1 mol.) and a carefully acidified alcoholic solution of diethyl γ -aminobutyraldehyde (1 mol.), and allowing reaction to proceed at room temperature for three days. The bases of type (VIII) produced could not be purified by distillation, even *in vacuo*, but it was possible by acid hydrolysis to eliminate one or both of the carbethoxyl groups. The ketones (XII) obtained by complete removal of the ester groups were usually capable of distillation under reduced pressure. Clemmensen reduction converted them into the

mono-substituted octahydropyrrocolines (XIII), colourless unstable oils which rapidly darken on exposure to light and



XII.



XIII.

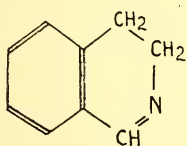
air. In them the nitrogen atom is definitely tertiary (lack of reactivity to nitrous acid, and ready formation of deliquescent methiodides). Usually it was possible to isolate two isomeric picrates from each of these bases, of which ($R \neq H$) there are, theoretically, four forms (cf. Clemo, Morgan and Raper, *J.C.S.*, 1935, 1743). An exhaustive stereochemical study of the bases available by this method of synthesis has not yet been undertaken, but it is hoped to report the results of such work later.

Altogether, the condensation of five aldehydes, viz. formaldehyde, acetaldehyde, iso-butyraldehyde, benzaldehyde, and piperonal—with γ -aminobutyraldehyde and acetone dicarboxylic ester was studied. All of these, with the exception of piperonal, yielded products of the expected type, the best result being obtained with acetaldehyde. Piperonal gave no octahydropyrrocoline base, and the yield in the benzaldehyde condensation was not good—suggesting that the reaction proceeds better with aliphatic aldehydes than with aromatic.

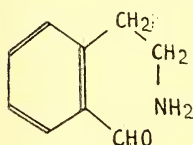
Previous methods of synthesis in the octahydropyrrocoline series (cf. e.g. Clemo and Ramage, *J.C.S.*, 1932, 2969; Clemo, Morgan and Raper, *J.C.S.*, 1935, 1743; Clemo, Metcalfe and Raper, *J.C.S.*, 1936, 1429; Clemo and Metcalfe, *J.C.S.*, 1937, 1518; Diels and Alder, *Annalen*, 1933, 505, 103-50; Diels and Meyer, *ibid.*, 1934, 513, 129; Diels and Moller, *ibid.*, 1935, 516, 45) have involved fairly long series of reactions; and, generally speaking, have not rendered available derivatives with substituents in the piperidine ring. The present method readily allows of the introduction of a substituent in the 5-position; whilst the carbonyl group in the 7-position in the bases (XII) renders possible the introduction of alkyl substituents on the

7-carbon atom by methods similar to those employed by Clemo and Metcalfe (*loc. cit.*). Further, the utilisation of substituted γ -aminobutyraldehydes (e.g. β -methyl- γ -aminobutyraldehyde, available via crotonaldehyde) renders possible the synthesis of octahydropyrrocolines with substituents in both rings. It is hoped to report the results of experiments designed to test these suggested methods soon.

Finally, it should be pointed out that substances of the 3:4-dihydroisoquinoline (XIV) type may be looked on as Schiff's bases derived from δ -amino-aldehydes. In the

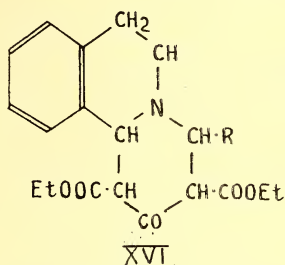


XIV



XV

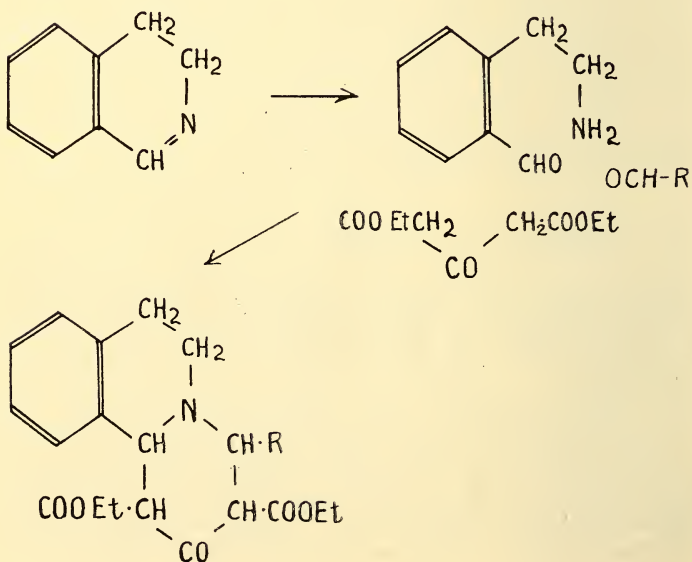
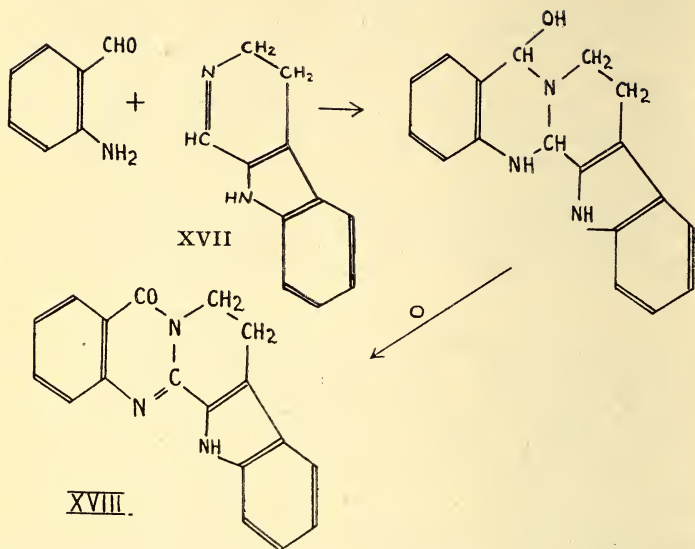
open form (XV), they should be capable of reacting with acetone dicarboxylic ester in presence of an aldehyde to give bases of the type (XVI).



XVI

Now Schöpf has shown that it is possible to synthesise rutæcarpin in good yield from dihydro norharman (XVII) by condensation at room temperature with *o*-aminobenzaldehyde in aqueous solution at pH 5, followed by oxidation.

It would therefore seem more than probable that 3:4-dihydroisoquinoline, under the right conditions, is capable of functioning similarly to dihydro norharman and that reactions such as those represented by the scheme suggested below ought to be readily possible. It is proposed to test this hypothesis in the near future.



EXPERIMENTAL.

The general method of condensation employed for the preparation of octahydropyrrocoline derivatives was as follows: a solution of γ -aminobutyraldehyde diethylacetal (Manske, *Can. Journ. Research*, 1931, 5, 592; 1 mol.) in four times its volume of alcohol was made just acid to methyl orange with dilute hydrochloric acid, and then diethyl acetonedicarboxylate (1 mol.) and an aldehyde (R-CHO; 1 mol.) were added without delay. The homogeneous reaction mixture was then allowed to stand at room temperature for three days, after which a slight excess of solid sodium carbonate was added. The 5-R-7-keto-6:8-dicarbethoxy octahydropyrrocoline usually separated out within 30 minutes as an oil, or, as in the instance of 5-methyl-7-keto-6:8-dicarbethoxy octahydropyrrocoline as a crystalline solid. After allowing the reaction mixture to stand for a further day at room temperature the product was collected in ether solution and this was freed from alcohol by several washings with water. Drying with anhydrous sodium sulphate followed by removal of the ether left the primary condensation product as an oil, or as a crystalline solid. These primary condensation products—5-substituted-7-keto-6:8-dicarbethoxy-octahydropyrrocoldines—could not be distilled, even *in vacuo*, without decomposition.

To obtain (a) the monocarbethoxy 5-substituted-7-keto-octahydropyrrocoline, (b) the 5-substituted-7-keto-octahydropyrrocoline, or (c) the 5-substituted octahydropyrrocoline, the ethereal solution of the primary condensation product was extracted with dilute (1:1) hydrochloric acid (100-200 c.c. for 1/10th gram—molecular quantities). Refluxing of this acid extract (A) for two hours (until evolution of carbon dioxide had practically ceased) led to elimination of one carbethoxyl group. The resulting 5-substituted-7-keto-monocarbethoxyl-octahydropyrrocoline base was then recovered from the cooled acid solution by making alkaline and taking the base up and drying it in ether. The product was finally distilled under diminished pressure.

If after two hours' refluxing of the acid extract (A) a little amalgamated zinc was added, and the refluxing continued for a further six hours, the second carbethoxyl group was eliminated, and cooling, rendering of the solution alkaline, and extraction with ether yielded the

5-substituted-7-keto-octahydropyrrocoline which was purified by vacuum distillation.

If the acid extract (A) was refluxed for two hours, a little amalgamated zinc added and refluxing continued for a further two hours, and then more amalgamated zinc (approx. 50 g. for 1/10th gram—molecular quantities) added, and refluxing continued until most of the zinc had dissolved, decarboxylation and reduction were complete and it was possible to recover the 5-substituted-octahydropyrrocoline base from the cooled solution by treatment with 20% sodium hydroxide solution followed by either steam distillation (especially for 5-alkyl-octahydropyrrocolines) or ether extraction. The oily base was eventually distilled *in vacuo*.

The oily bases obtained by the above described methods are all unstable in varying degree and darken when exposed to light and air. All possess extremely bitter tastes, and the volatile bases have a rather unpleasant odour in the crude state. When freshly distilled they have a characteristic stupefying basic odour, and fume readily in presence of hydrogen chloride.

By addition of a deficiency of alcoholic picric acid solution to each base a solid product was usually obtained from which repeated recrystallisation usually provided a pure specimen of the picrate of one of the cis-trans forms of the base. Addition of excess picric acid to the filtrate from this first picrate usually led to precipitation of the picrate of the second isomer which, also, could be purified by repeated recrystallisation.

7-Keto-6 : 8-Dicarbethoxy-Octahydropyrrocoline.

Diethyl acetonedicarboxylate (12.2 g.), formaldehyde (4.5 c.c. of 40% solution) and γ -aminobutyraldehyde (9.6 g.) gave 7-keto-2 : 6-dicarbethoxy octahydropyrrocoline (15 g.; 88% of theory) as a pale yellow oil which could not be distilled, and gave only gummy picrates.

7-Keto-6 (or 8)-Carbethoxy-Octahydropyrrocoline.

This base was obtained by 2 hours acid hydrolysis of the crude 7-keto-6 : 8-dicarbethoxy-octahydropyrrocoline described above as a colourless oil boiling at 131.5°/1 mm. It crystallised on standing, and was obtained in colourless needles melting at 60° after recrystallisation from petroleum ether. The yield (calculated on the original condensation) was only 12% of theory.

Found: C=62.5, H=8.0%; calculated for $C_{11}H_{17}O_3N$, C=62.5, H=8.0%.

The *picrate*, yellow needles from water, melts at 137°.

Found: N=12.2%; calculated for $C_{17}H_{20}O_{10}N_4$, N=12.8%.

7-Keto-Octahydropyrrocoline.

Hydrolysis of 7-keto-6:8-dicarbethoxy octahydropyrrocoline for 8 hours in presence of a little amalgamated zinc led to decarbethoxylation and formation of 7-keto-octahydropyrrocoline (2 g.; 24% of theory, calculated on the original condensation). It was an oil boiling at 104.5°/18 mm.

Found: C=68.8, H=9.3%; calculated for $C_8H_{13}ON$, C=69.1, H=9.4%.

The *picrate* obtained in golden tetrahedra from water, melted (with decomposition) at 198-200°.

Found: N=15.2%; calculated for $C_{14}H_{16}O_8N_4$, N=15.2%.

Octahydropyrrocoline.

Prolonged hydrolysis and reduction of the crude 7-keto-6:8-dicarbethoxy octahydropyrrocoline by the general method led to formation of octahydropyrrocoline (3 g.; 40% of theory, calculated on the original condensation). It was a colourless oil boiling at 60°/15 mm.

Found: C=76.4, H=11.8%; calculated for $C_8H_{15}N$, C=76.8, H=12.0%.

The *picrate*, long yellow needles from water, melted (with decomposition) at 215°.

Found: N=15.6%; calculated for $C_{14}H_{18}O_7N_4$, N=15.8%.

The *platinichloride*, orange rhombohedra from water, melted at 203° (with decomposition).

5-Methyl-7-keto-6:8-Dicarbethoxy Octahydropyrrocoline.

From diethyl acetonedicarboxylate (12.2 g.), acetaldehyde (2.6 g.) and γ -aminobutyral (9.6 g.) was isolated a crude product consisting mainly of crystals with a little oil (17 g.; 95% of theory). After recrystallisation from petroleum ether felted white needles (14 g.) melting at 102° were obtained.

Found: C=60.3, H=8.1%; calculated for $C_{15}H_{23}O_5N$, C=60.6, H=8.6%.

The *picrate*, yellow plates from benzene, melted at 150°.

Found: N=10.8%; calculated for $C_{21}H_{26}O_{12}N_4$, N=10.6%.

5-Methyl-7-Keto-Octahydropyrrocoline.

Hydrolysis with hot dilute hydrochloric acid for two hours, followed by addition of a little zinc amalgam and a further six hours refluxing of the recrystallised 5-methyl-7-keto-6:8-dicarbethoxy-octahydropyrrocoline just described led to decarbethoxylation and formation of 5-methyl-7-keto-octahydropyrrocoline. It was isolated as a colourless oil (6 g.; 60% of theory, calculated on the original condensation) boiling at 119°/20 mm.

Found: C=70.4, H=10.0%; calculated for $C_9H_{15}ON$, C=70.6, H=9.8%.

Two *picrates* were obtained from this oil. The first, recrystallised from water, formed long slender needles melting at 194° (with decomposition).

Found: N=14.8%; calculated for $C_{15}H_{18}O_8N_4$, N=14.7%.

The second was obtained in yellow leaflets melting and decomposing at approximately 188°, but it could not be completely freed from the other isomer.

Found: N=14.8%; calculated for $C_{15}H_{18}O_8N_4$, N=14.7%.

5-Methyl-Octahydropyrrocoline.

This base was obtained by the standard acid hydrolysis and reduction procedure described above, from the recrystallised 5-methyl-7-keto-6:8-dicarbethoxy octahydropyrrocoline; and was isolated as a colourless oil (5 g.; 63% of theory calculated on the original condensation) boiling at 79°/15 mm.

Found: C=77.3, H=11.9%; calculated for $C_9H_{17}N$, C=77.7, H=12.2%.

Two *picrates* could be isolated. Of these the first formed fine yellow needles (from water) melting at 235° (with decomposition).

Found: N=15.2%; calculated for $C_{15}H_{20}O_7N_4$, N=15.2%.

The second *picrate* formed long yellow needles (from water) melting at 196° (with decomposition).

Found: N=15.4%; calculated for $C_{15}H_{20}O_7N_4$, N=15.2%.

The *platinichloride*, orange truncated prisms from water, softens at 170° and decomposes at 220°.

5 - Isopropyl - 7 - Keto - 6 : 8 - Dicarbethoxy - Octahydro-pyrrocoline.

Condensation together of diethyl acetonedicarboxylate (12.2 g.), isobutyraldehyde (4.3 g.) and γ -aminobutyral acetal (9.6 g.) in alcohol (40 c.c.) gave 5-isopropyl-7-keto-6:8-dicarbethoxy octahydro-pyrrocoline as a pale yellow oil (18 g.; 95% of theory) which could not be distilled, or induced to crystallise. However, it readily yielded a *picrate* which was obtained in yellow cubes melting at 135° after recrystallisation from a benzene-petroleum ether mixture.

Found: N=10.0%; calculated for $C_{23}H_{30}O_{12}N_4$, N=10.1%.

5-Isopropyl-Octahydro-pyrrocoline.

Complete hydrolysis and Clemmensen reduction of the above described crude 5-isopropyl-7-keto-6:8-dicarbethoxy octahydro-pyrrocoline yielded the oxygen-free base—5-isopropyl-octahydro-pyrrocoline as a colourless oil (5 g.; 50% of theory, calculated on the original condensation) distilling at 99-101°/23 mm.

Found: C=78.8, H=12.3%; calculated for $C_{11}H_{21}N$, C=79.0, H=12.6%.

The base yielded only oily red *picrates* but a crystalline yellow *picrolonate* (leaflets from water) was obtained. It melted at 197° (with decomposition).

Found: N=16.4%; calculated for $C_{21}H_{29}O_5N_5$, N=16.2%.

5-Phenyl Octahydro-pyrrocoline.

Condensation together of diethyl acetone dicarboxylate (12.2 g.), benzaldehyde (6.4 g.) and γ -aminobutyral acetal (9.6 g.) in alcohol (40 c.c.) led to formation of 5-phenyl-7-keto-6:8-dicarbethoxy octahydro-pyrrocoline together with several other products. It was not possible to isolate this substance in the pure condition. Consequently, the crude oily condensation product was hydrolysed and reduced by the standard method to 5-phenyl octahydro-

pyrrocoline which was isolated as a colourless oil (2 g.; 16% of theory) boiling at 155°/20 mm., and possessing a mouse-like odour.

Found: C=83.1, H=9.1%; calculated for $C_{14}H_{19}N$, C=83.6, H=9.5%.

Two *picrates* were isolated from this base. The first, obtained in pale yellow rectangular blocks from water, melted at 174°.

Found: N=12.9%; calculated for $C_{20}H_{22}O_7N_4$, N=13.0%.

The second *picrate* crystallised from benzene in yellow rhombohedra melting at 193°.

Found: N=13.1%; calculated for $C_{20}H_{22}O_7N_4$, N=13.0%.

ACKNOWLEDGMENT.

The authors desire to express their grateful thanks to Miss D. Little, B.Sc., for most of the (semi-micro) analyses recorded in this paper.

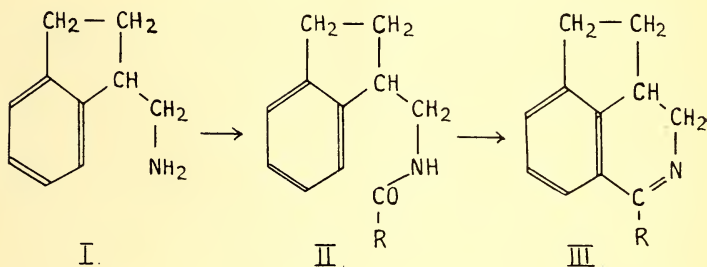
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4 : 5-ETHYLENE-ISO-QUINOLINE DERIVATIVES.

By ARTHUR FLACK, B.Sc.,
and FRANCIS LIONS, B.Sc., Ph.D.

(Manuscript received, November 22, 1939. Read, December 6, 1939.)

α -Hydrindylmethylamine (I) may be regarded as a substituted β -phenylethylamine whose acyl derivatives (II) should be capable of conversion to the corresponding dihydroisoquinolines (III) by suitable application of the Bischler-Napieralski synthesis.

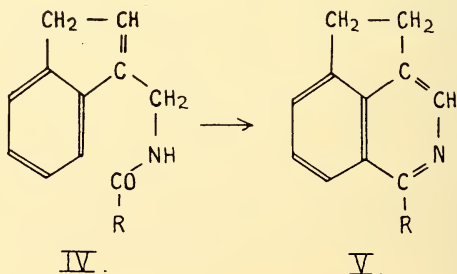


The experimental work described in this paper has established that it is possible to prepare 1-phenyl-3:4-dihydro-4:5-ethylene isoquinoline (III; $\text{R} = -\text{C}_6\text{H}_5$) and 1-methyl-3:4-dihydro-4:5-ethylene isoquinoline (III; $\text{R} = -\text{CH}_3$) by treatment of the corresponding benzoyl α -hydrindylmethylamine (II; $\text{R} = -\text{C}_6\text{H}_5$) and acetyl α -hydrindylmethylamine (II; $\text{R} = -\text{CH}_3$) with phosphorus pentoxide in hot xylene (cf. e.g. Späth and Polgar, *Monats.*, 1929, 51, 197; Späth, *Ber.*, 1930, 63, 2098; *Annalen*, 1913, 395, 299, 335; *Berichte*, 1909, 42, 1973, 2075, 2943), or with phosphorus oxychloride (cf. e.g. Buck, Perkin and Stevens, *J.C.S.*, 1925, 1462; Halin and Ludewig, *Berichte*, 1934, 67, 2031). The yields of cyclic bases (III) were approximately the same by either method and were very poor. No isoquinoline could be obtained in similar experiments with formyl α -hydrindylmethylamine (II; $\text{R} = -\text{H}$).

The low yields obtained may well be accounted for by the peculiar stereochemical configurations of the bases (III). It is most probable that in them the five-membered ring is planar and lies in the plane of the benzene ring (cf. Jackson and Kenner, *J.C.S.*, 1928, 573; Lions and Ritchie, *THIS JOURNAL*, 1939, 73, 125-149). Carbon atom I should also lie in this plane. The carbon atom 4 is asymmetric; and this asymmetry, coupled with its position in the plane of the benzene ring necessitates that carbon atom 3, and possibly, also, the nitrogen atom of the pyridine ring, must lie to one or other side of this plane—leading to a "puckered" dihydropyridine ring. Resolution of one or other of the bases III would establish this point, but, unfortunately, lack of material has precluded resolution experiments.

1-Methyl-3 : 4-dihydro-4 : 5-ethylene isoquinoline (III; $R = -CH_3$) has been shown to be readily reducible to the corresponding tetrahydro-base (IV) with sodium and alcohol. Attempts to prepare (IV) from (I) by condensation with acetaldehyde in presence of hydrochloric acid (cf. e.g. Pictet and Spengler, *Berichte*, 1911, 44, 2030; Decker and Becker, *Annalen*, 1913, 395, 346-362; Späth and Berger, *Berichte*, 1930, 63, 2098), or under physiological conditions (cf. e.g. Schöpf and Bayerle, *Annalen*, 1934, 513, 196; Halin and Ludewig, *Berichte*, 1934, 67, 2031; Hahn and Schale, *ibid.*, 1935, 68, 24; Späth and Kuffner, *ibid.*, 1936, 69, 378) all proved abortive.

Finally, it should be noted that if the low yields of dihydroisoquinoline bases obtained by cyclisation of acyl-1-hydrindyl-methylamines are due to the steric factors considered, it should be readily possible to effect cyclisation of acyl-1-indenyl methylamines (IV) to the corresponding 4 : 5-ethylene isoquinolines (V), whose molecules should be planar.



The results of experiments designed to study this hypothesis will be reported later.

EXPERIMENTAL.

1-Aminomethyl hydrindene (I).

v. Braun (*Berichte*, 1917, 50, 59) has recorded the preparation of 1-aminomethyl hydrindene (α -hydrindyl methylamine). The base used in the experiments described below was prepared as follows: Sodio malonic ester was condensed with ethyl cinnamate to triethyl β -phenyl propane- α : γ : γ -tricarboxylate (cf. Michael, *Amer. Chem. Journ.*, 1887, 9, 115; *J. Pr. Chem.*, 1887 (2), 35, 352). This ester was hydrolysed to the corresponding acid, which was then decarboxylated to β -phenylglutaric acid (cf. Avery and Bouton, *Amer. Chem. Journ.*, 1898, 20, 511), and this was cyclised to 1-hydrindone-3-acetic acid, subjection of the ester of which to the Buchner-Curtius degradation led ultimately to the required 1-hydrindyl methylamine, a colourless oil boiling at 103-105°/4 mm. It readily formed a crystalline hydrochloride, which melted at 211° after recrystallisation from absolute alcohol.

Attempts to prepare the base directly from hydrindene-1-acetic acid with hydrazoic acid in presence of sulphuric acid (cf. Schmidt, *Berichte*, 1924, 57, 704; v. Braun, *Annalen*, 1931, 490, 125; Oesterlin, *Zeit. Angew. Chem.*, 1932, 45, 536) were unsuccessful.

The *dinitrophenylhydrazone* of 1-hydrindone-3-acetic acid prepared in the usual manner was obtained from acetic acid in orange-red prisms melting at 242°.

1-Formylaminomethyl Hydrindene (II; R=H).

The base (I) (5 g.) was carefully dissolved in anhydrous formic acid (30 cc.), much heat being evolved. The solution was heated under reflux for 12 hours, and then distilled (finally *in vacuo*). The formyl derivative (II; R=H; 5.3 g.) was obtained as a viscous, colourless oil boiling at 190-195°/4.5 mm.

Found: C=75.1, H=7.1%; calculated for C₁₁H₁₃ON, C=75.4, H=7.4%.

1-Acetylaminomethylhydrindene (II; R=CH₃).

The base (I) (10 g.) was readily acetylated with acetic anhydride in the usual manner. The acetyl derivative

II; $R=CH_3$; 12 g.) distilled at $180-182^\circ/4$ mm. as a colourless viscous oil.

Found: $C=76.0$, $H=8.0\%$; calculated for $C_{12}H_{15}ON$, $C=76.2$, $H=7.9\%$.

1-Benzoylaminomethylhydrindene (II; $R=C_6H_5$).

Application of the Schotten-Baumann reaction to the base (I) (10 g.) gave the crystalline benzoyl derivative (II; $R=C_6H_5$; 13.5 g.). Recrystallised from aqueous alcohol it formed colourless prisms melting at 115° .

Found: $N=5.3\%$; calculated for $C_{17}H_{17}ON$, $N=5.6\%$.

1-Phenyl-4 : 5-Ethylene-3 : 4-Dihydro-iso-Quinoline (III; $R=C_6H_5$).

Phosphorus pentoxide powder (24 g.) was added to a solution of 1-benzoyl-aminomethylhydrindene (10 g.) in dry xylene and the mixture boiled under reflux for 30 minutes. After pouring off the xylene the sticky residue was taken up in ice-water and the resulting cold acid solution washed several times with ether. It was then made alkaline with sodium hydroxide solution and the liberated base collected and dried in ether. After removal of the solvent it was distilled *in vacuo* and obtained as a pale yellow viscous liquid (2.5 g.) boiling at $204-206^\circ/6$ mm., which was induced to crystallise. Slow evaporation of its solution in petroleum ether yielded crystals melting at $52-54^\circ$.

Found: $C=86.9$, $H=6.3\%$; calculated for $C_{17}H_{15}N$, $C=87.5$, $H=6.5\%$.

The *picrate*, yellow prisms from alcohol, melted at 181° .

Found: $N=11.9\%$; calculated for $C_{23}H_{18}O_7N_4$, $N=12.1\%$.

The *methiodide*, large yellow crystals from an alcohol-ethyl acetate mixture, melted at $217-218^\circ$.

Found: $C=57.2$, $H=4.8\%$; calculated for $C_{18}H_{18}NI$, $C=57.6$, $H=4.8\%$.

1-Methyl-4 : 5-Ethylene-3 : 4-Dihydro-iso-Quinoline (III; $R=CH_3$).

This base (2 g.) was obtained from 1-acetylaminomethylhydrindene (12 g.) with phosphorus pentoxide (23 g.) in boiling xylene (115 cc.) exactly as described for the 1-phenyl derivative described above. It was obtained as a pale yellow oil boiling at $145-150^\circ/20$ mm. which readily

darkened in colour. It was analysed as the *picrate*, yellow needles from alcohol, melting at 211°.

Found : N=13.8% ; calculated for $C_{18}H_{16}O_7N_4$, N=14.0%.

The *methiodide*, twice recrystallised from ethyl alcohol-ethyl acetate mixture melted at 114°.

Found : N=4.6% ; calculated for $C_{13}H_{16}NI$, N=4.5%.

The *hydrochloride* melted at 238-240°.

Found : C=70.7, H=7.1% ; calculated for $C_{12}H_{14}NCl$, C=71.2, H=7.0%.

The base III ($R=CH_3$) could also be obtained in small yield by a method similar to that employed by Buck, Perkin and Stevens (*J.C.S.*, 1925, 1462), viz. heating of a solution of the amide (II) ($R=CH_3$) with phosphorus oxychloride (18 c.c.) and toluene (80 c.c.) under reflux for 50 minutes. After removal of the toluene, etc., *in vacuo*, the residue was taken up in dilute acetic acid, the solution well washed with ether, then basified with ammonia and the base recovered with the help of ether.

1-Methyl-4 : 5-Ethylene-1 : 2 : 3 : 4-Tetrahydro-iso-Quinoline.

Sodium (5 g.) was added to a boiling solution of the base (III) ($R=CH_3$) (0.8 g.) in absolute ethyl alcohol (60 c.c.). When the metal had dissolved completely most of the alcohol was removed with steam, and the base recovered from the cooled alkaline solution with the help of ether. It distilled between 110° and 120° at 4 mm. Its *hydrochloride* formed colourless stout needles from an alcohol-ethyl acetate mixture and melted at 209-210°.

Found : C=68.2, H=7.8% ; calculated for $C_{12}H_{16}NCl$, C=68.7, H=7.6%.

ACKNOWLEDGMENT.

Most of the (micro)analyses recorded in this paper were carried out by Miss D. Little, B.Sc., whose assistance is gratefully acknowledged.

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DERIVATIVES OF 4-HYDROXY-QUINOLINE.*

PART II.

By RICHARD GILLIS,
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(Manuscript received, November 22, 1939. Read, December 6, 1939.)

The elegant method of synthesis of 4-hydroxyquinoline derivatives devised by Conrad and Limpach (*Berichte*, 1887, 20, 944, 948; cf. also Limpach, *ibid.*, 1931, 64, 969-70), in which a primary arylamine is condensed in the cold with a β -ketonic ester to a β -arylamino- α - β -unsaturated ester, which is then cyclised to the required quinoline derivative by heating to 250-280°, is not always readily available for the synthesis of 4-hydroxyquinolines with substituent alkyl groups in the 3-position. It is true that α -alkyl- α -acyl acetic esters can often be induced to react in the cold with arylamines, water being eliminated and α -alkyl- β -arylamino- α - β -unsaturated esters being formed; and these in turn can be cyclised readily to 2:3-disubstituted 4-hydroxy-quinolines. Thus, Conrad and Limpach (*Berichte*, 1891, 24, 2990) were able to prepare 2:3-dimethyl-4-hydroxyquinoline and 2-methyl-3-ethyl-4-hydroxyquinoline from aniline and ethyl α -acetylpropionate and ethyl α -acetylbutyrate respectively. Kermack and Smith (*J.C.S.*, 1930, 2205; 1931, 221) condensed p-anisidine with ethyl α -acetyl propionate to ethyl α -methyl- β (p-anisidino)-crotonate which was then cyclised to 2:3-dimethyl-4-hydroxy-6-methoxy quinoline. Also, Blount, Perkin and Plant (*J.C.S.*, 1929, 1977) showed that aniline condenses fairly readily in the cold with ethyl cyclopentanone-2-carboxylate and with ethyl cyclohexanone-2-carboxylate to give the corresponding ethyl 1-anilino- $\Delta^{1:2}$ -cyclopentene-2-carboxylate and ethyl 1-anilino- $\Delta^{1:2}$ -cyclohexene-2-carboxylate respectively, which could then be readily cyclised (cf. also Sen and Basu, *Journ. Indian Chem. Soc.*,

* Part I appeared in THIS JOURNAL, 1937-38, 71, 458.

1930, 7, 435; Hughes and Lions, *THIS JOURNAL*, 1937-38, 71, 458).

On the other hand α -alkyl- α -acyl acetic esters are often very reluctant to react with primary arylamines, and attempts to force condensation by heating lead to interaction of the arylamine with the ester group and formation of α -alkyl- α -acyl acetanilides, or even symmetrical ureas, the ester group being completely eliminated. Examples of this type of reaction have been frequently reported (cf. e.g. Knorr, *Annalen*, 1888, 245, 358 *seq.*; Foglino, *Ann. Chem. Pharm.*, 1898, 26, 535; Guareschi, *Chem. Zentr.*, 1905, 11, 685; Jadhar, *Journ. Indian Chem. Soc.*, 1931, 8, 681).

In view of the ease of formation of β -arylamino- α - β -unsaturated esters from arylamines and unsubstituted acyl acetic esters it seemed probable to the authors that a general method of synthesis of 2:3-disubstituted-4-hydroxyquinoline derivatives would be afforded by suitable alkylation of these readily accessible β -arylamino- α - β -unsaturated esters prior to their cyclisation by heat to quinolines. The alkylation of β -aminocrotonic esters, and of nitrogen substituted β -aminocrotonic esters has been frequently studied (cf. e.g. Collie, *Annalen*, 1884, 226, 316; Conrad and Epstein, *Berichte*, 1887, 20, 3055; Robinson, *J.C.S.*, 1916, 109, 1038); and the attachment of the entering alkyl group to the α -carbon atom of the crotonic acid residue in such processes is well established. In particular, Conrad and Limpach (*Berichte*, 1891, 24, 2990) have already shown that ethyl β -anilino crotonate can be readily methylated and ethylated to ethyl α -methyl- β -anilino crotonate, and ethyl α -ethyl- β -anilino crotonate respectively, which, in turn, were cyclised to 2:3-dimethyl-4-hydroxyquinoline and 2-methyl-3-ethyl-4-hydroxyquinoline. The scheme of reactions is shown on p. 262.

A further example of the same process was recorded by Mander-Jones and Trikojus (*THIS JOURNAL*, 1932, 66, 309), who allylated the same ester.

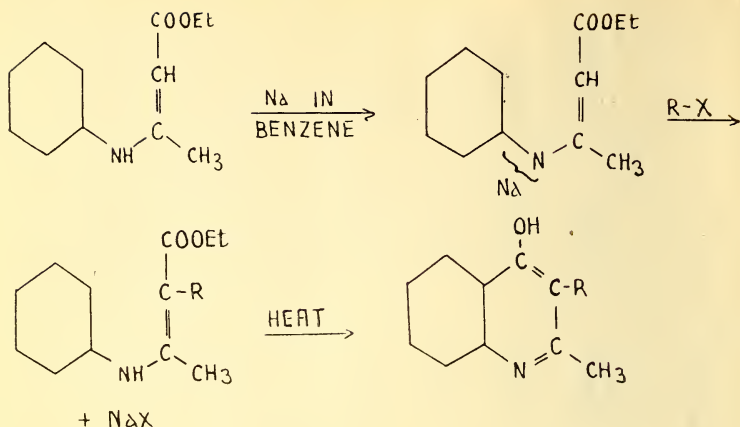
The present paper records the results of several experiments designed to prove the general availability of this method for the production of 2:3-disubstituted-4-hydroxyquinolines. Two β -aryl-amino-crotonic esters—viz. ethyl β -anilino crotonate and ethyl β -(2-naphthylamino)-crotonate—were prepared by the method of Coffey, Thomson and Wilson (*J.C.S.*, 1936, 856), and alkylated by the following process: The arylaminocrotonic ester

2-METHYL-3-ALKYL-4-HYDROXYQUINOLINES.

Substituent in 3-position.	Crystalline Form.	Solvent of Re- crystallisation.	M.P.	Molecular Formula.	Analysis.	
					Found.	Calculated.
Methyl	Prisms.	Acetone.	217°	$C_{11}H_{11}ON$	C=76.1 H= 6.3	C=76.3 H= 6.4
Ethyl	Leaflets.	Methanol.	275°	$C_{12}H_{13}ON$	C=76.7 H= 7.1	C=77.0 H= 7.0
n-Propyl	Needles.	Acetone.	263°	$C_{13}H_{15}ON$	C=77.5 H= 7.6	C=77.6 H= 7.5
Allyl	Prisms.	Methanol.	273°	$C_{13}H_{13}ON$	C=78.1 H= 6.5	C=78.4 H= 6.5
Butyl	Prisms.	Acetone.	237°	$C_{14}H_{17}ON$	C=77.6 H= 7.7	C=78.1 H= 7.9

2-METHYL-3-ALKYL-4-HYDROXY-5:6-BENZOQUINOLINES.

Substituent in 3-position.	Crystalline Form.	Solvent of Re- crystallisation.	M.P.	Molecular Formula.	Analysis.	
					Found.	Calculated.
Methyl	Needles.	Ethanol.	> 300	C ₁₃ H ₁₃ ON	C = 80.5 H = 5.9	C = 80.7 H = 5.8
Ethyl	Prisms.	—	..	C ₁₆ H ₁₅ ON	C = 81.3 H = 6.1	C = 81.0 H = 6.3
n-Propyl	Rods.	—	..	C ₁₇ H ₁₇ ON	C = 81.0 H = 7.0	C = 81.2 H = 7.0
iso-Propyl	Rods.	—	..	C ₁₇ H ₁₇ ON	C = 81.1 H = 6.8	C = 81.2 H = 7.0
Butyl	Rods.	—	..	C ₁₈ H ₁₉ ON	C = 81.2 H = 7.4	C = 81.5 H = 7.2
Benzyl	Prisms.	—	..	C ₂₁ H ₁₇ ON	C = 84.0 H = 5.9	C = 84.3 H = 5.7
β-Phenyl ethyl	Prisms.	—	..	C ₂₂ H ₁₉ ON	C = 83.9 H = 6.0	C = 84.3 H = 6.1



(0.05 gram mol.) was added to a cooled solution of sodium (1.1 g.; 0.05 mol.) in absolute ethyl alcohol (60 c.c.), and then, after standing 10-20 minutes, the alkyl halide (0.05 mol.) was added and the mixture heated under reflux for three hours. The cooled solution was then poured into water and the precipitated oil taken up and dried in ether, and the solvent removed. The residual oily ester was then poured into 8 times its weight of paraffin oil (which had been preheated to 260°). The quinoline base which separated was then collected and purified by the usual methods. The previous tables summarise the results obtained.

The yields varied between 50% and 90% of theory. *Bis-(2-methyl-4-hydroxy-5:6-benzo-5-quinolyl)-ethane* prisms (from much alcohol) melting above 300° was also prepared by the standard method from β -(2-naphthylamino)-crotonic ester and ethylene dibromide.

Found: C=81.0, H=5.6%; calculated for $\text{C}_{30}\text{H}_{24}\text{O}_2\text{N}_2$, C=81.1, H=5.4%.

ACKNOWLEDGMENT.

The authors gratefully acknowledge the assistance of Miss D. Little, B.Sc., for most of the (semi-micro) analyses recorded in this paper.

Department of Organic Chemistry,
The University of Sydney.

ABSTRACT OF PROCEEDINGS

OF THE

Royal Society of New South Wales*April 5, 1939.*

The Annual Meeting, being the five hundred and sixty-seventh General Monthly Meeting of the Society, was held in the Hall of Science House, Gloucester and Essex Streets, Sydney, at 7.45 p.m.

Professor J. C. EARL, President, was in the chair. Thirty-four members and seven visitors were present. The minutes of the general monthly meeting of December 7th, 1938, were read and confirmed.

The following gentlemen were elected officers and members of the Council for the coming year :

President :

H. S. HALCRO WARDLAW, D.Sc., F.A.C.I.

Vice-Presidents :

PROF. J. C. EARL, D.Sc., Ph.D.

R. J. NOBLE, M.Sc., Ph.D., B.Sc.Agr.

W. L. WATERHOUSE, M.C.,

R. W. CHALLINOR, F.I.C., F.C.S.

D.Sc.Agr., D.I.C., F.L.S.

Honorary Secretaries :

PROF. A. P. ELKIN, M.A., Ph.D.

C. ANDERSON, M.A., D.Sc.

Honorary Treasurer :

M. B. WELCH, B.Sc., A.I.C.

Members of Council :PROF. V. A. BAILEY, M.A.,
D.Phil., F.Inst.P.

W. R. BROWNE, D.Sc.

EDWIN CHEEL.

PROF. L. A. COTTON, M.A.,
D.Sc.PROF. C. E. FAWSITT, D.Sc.,
Ph.D.PROF. J. MACDONALD
HOLMES, Ph.D., F.R.G.S.,
F.R.S.G.S.

D. P. MELLOR, M.Sc.

H. G. RAGGATT, M.Sc.

PROF. O. U. VONWILLER,
B.Sc., F.Inst.P.

L. L. WATERHOUSE, B.E.

The Annual Balance Sheet and Revenue Account were submitted to members by the Honorary Treasurer, and on the motion of Mr. Welch, seconded by Mr. Cheel, were adopted.

THE ROYAL SOCIETY OF NEW SOUTH WALES.

BALANCE SHEET AS AT 28th FEBRUARY, 1939.

		LIABILITIES.			
1938.		1939.			
£		£	s. d.	£	s. d.
	Trust Funds—				
	Clarke Memorial Fund ..	1,689	1 9		
	Walter Burfitt Prize Fund	636	8 8		
	Liversidge Bequest ..	676	8 7		
3,040				3,001	19 0
10	Subscriptions Paid in Advance			6	6 0
6	Sundry Liabilities			0	0 0
	Provision for Unexpired Pro- portion of Life Membership				
155	Subscriptions			167	0 0
26,570	Accumulated Fund			26,669	11 6
<u>£29,781</u>				<u>£29,844</u>	<u>16 6</u>

ABSTRACT OF PROCEEDINGS.

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1938.	ASSETS.	1939.		
£		£	s.	d.
	Cash at Bank and on Hand—			
	The Union Bank of Australia Ltd.	86	7	2
	Commonwealth Savings Bank of Australia	311	2	5
	Petty Cash	1	16	3
630				399 5 10
	Bonds and Inscribed Stock—			
	Commonwealth Bonds (Face Value £4,340)	4,291	10	0
	Commonwealth Stock (Face Value £2,900)	2,947	6	3
	Rural Bank of New South Wales Stock (Face Value £320)	300	0	0
7,239				7,538 16 3
	Science House Management Committee—			
14,590	Payments to date			14,590 0 0
	Sundry Debtors—			
	Subscriptions Unpaid	308	1	0
	Less Reserve	308	1	0
				0 0 0
6,800	Library			6,800 0 0
	Furniture	435	1	0
	Less Depreciation written off	19	18	9
				415 2 3
	Add Additions	17	18	10
435				433 1 1
	Pictures	48	5	8
	Less Depreciation written off	2	4	0
48				46 1 8
	Microscopes	21	8	8
	Less Depreciation written off	1	0	0
21				20 8 8
	Lantern	18	1	0
	Less Depreciation written off	0	18	0
18				17 3 0
<u>£29,781</u>				<u>£29,844 16 6</u>

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 28th February, 1939, 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. We also have a certificate from the Rural Bank of New South Wales that stock to the face value of £320 is inscribed in the name of the Society.

HORLEY & HORLEY,
Chartered Accountants (Aust.).
(Sgd.) M. B. WELCH,
Hon. Treasurer.

National Mutual Building,
350 George Street,
Sydney, 21st March, 1939.

**REVENUE ACCOUNT FOR THE PERIOD ENDED
28th FEBRUARY, 1939.**

Year ended 31st March, 1938.		Period ended 28th February, 1939.					
£		£	s.	d.	£	s.	d.
3	To Advertising	2	10	0			
37	„ Cleaning	33	10	0			
27	„ Depreciation	24	0	9			
5	„ Electric Light and Gas	5	7	9			
14	„ Insurance	13	17	1			
86	„ Library Maintenance	60	0	10			
50	„ Miscellaneous Expenses	52	11	8			
262	„ Office Salaries and Audit Fees	235	17	0			
34	„ Office Sundries and Stationery	9	1	7			
81	„ Printing	165	1	5			
	„ Printing and Publishing						
196	Journal	451	8	10			
3	„ Repairs	4	13	9			
49	„ Stamps and Telegrams	52	3	4			
14	„ Telephone	11	6	7			
	„ Annual Dinner—						
83	Expenses .. £49 6 2						
46	Less Received 33 12 0						
—	37				15	14	2
	<hr/>						
898					1,137	4	9
	„ Balance, being Net Revenue for the Period, transferred to Accumulated Fund ..				90	5	2
	344						
	<hr/>						
	£1,242				£1,227	9	11

Year ended 31st March, 1938.		Period ended 28th February, 1939.					
£	£	£	s.	d.	£	s.	d.
	487	By Members' Subscriptions			488	5	0
	400	„ Government Subsidy			400	0	0
167		„ Science House Receipts	109	0	0		
39		Less Rent Paid	38	13	1		
—	128						
	<hr/>				70	6	11
	46	„ Miscellaneous Receipts			102	17	9
279		„ Interest Received	247	9	6		
		Less—					
		Clarke Memorial					
		Fund £63 4 0					
		Walter Burfitt					
		Prize Fund 24 6 9					
		Liversidge Be-					
		quest .. 23 18 6					
117							
—	162				111	9	3
	<hr/>						
		„ Proportion of Life Members'			136	0	3
		Subscriptions			30	0	0
	19						
	<hr/>						
	£1,242				£1,227	9	11

**ACCUMULATED FUND ACCOUNT FOR THE PERIOD
ENDED 28th FEBRUARY, 1939.**

	£	s.	d.
1939—February 28—			
To Arrears of Subscriptions, written off	21	0	0
„ Balance Carried Down	26,669	11	6
	<hr/>		
	£26,690	11	6
	<hr/>		
1938—March 31—	£	s.	d.
By Balance from last Account	26,569	13	4
1939—February 28—			
By Amount transferred from Bad Debts Reserve Account	26	9	0
„ Arrears of Subscriptions, written off, since recovered	4	4	0
„ Net Revenue for the Period	90	5	2
	<hr/>		
	£26,690	11	6
	<hr/>		
1939—February 28—			
By Balance Brought Down	£26,669	11	6

Mr. Cheel proposed and Mr. Sussmilch seconded a motion that Messrs. Horley & Horley should be reappointed as the Society's auditors for the year 1939-1940.

The Annual Report of the Council (1938-1939) was read, and on the motion of Mr. Cheel, seconded by Mr. Ollé, was adopted.

REPORT OF THE COUNCIL (RULE XXVI), 1938-1939.

We regret to report that we have lost by death ten members: Arthur Bayley, elected in 1935; Walter Blaxland, elected in 1888; James B. Brown, elected in 1906; Lindsay D. Cameron, elected in 1923; Harry Chambers Kent, elected in 1887; John Lane Mullins, elected in 1879; Prosper C. Trebeck, elected in 1879; George B. Vickery, elected in 1892; Fred Walsh, elected in 1903; and Percy Moore Wood, elected in 1891.

By resignation we have lost seven members: Sir Henry Barraclough, Edward F. Hallman, W. D. Mackenzie, Ruby Payne Scott, Henry G. Pyke, Andrew Reid, Frederick W. Wheatley.

Twelve ordinary members were elected during the year: Adrien Albert (life member), Marion Breckenridge, Francis P. Clune, S. Warren Carey (life member), Edward L. Griffiths, Christian W. J. Griffith, Dorothy Hill, Norman S. Noble, Una F. F. Pickard, Marie E. Phillips, John Wallis Powell, Thomas H. K. Sheahan.

Two members of over forty years' standing were elected life members, namely Harry C. Kent and Roland J. Pope. At the present time (March 31st) the membership stands at 266 ordinary members and seven honorary members.

During the Society's year there have been eight general meetings and ten meetings of the Council. Owing to the alteration in the date of

the Annual Meeting, the year consists on this occasion of eleven months, May 1st-March 31st. The average attendance at general meetings was 27, and at Council meetings it was 13.

Twenty-nine papers were read during the year, and at some of the meetings short talks were also given, namely :

- “ A Talk on his Experiences Abroad ”, by Professor J. C. Earl.
- “ Gleanings from a Hurried Visit to Great Britain ”, by Professor R. D. Watt.
- “ The Relations of Instinct and Thought Power in the Animal World ”, illustrated by a short film, by Mr. A. S. Le Souef.
- “ The Conquest of Malaria ”, by Dr. Adrien Albert.
- “ Wool Substitutes ”, by Mr. A. R. Penfold.
- “ Standardisation in Modern Life ”, by Mr. A. R. Hebblewhite.

Exhibits were shown by Mr. A. R. Penfold and Mr. E. Cheel.

Four Popular Science Lectures were given during the winter, and were all well attended by members of the Society and the general public :

- July 21st.—“ The Brain of Fossil Man ”, by Professor J. L. Shellshear, M.D., D.Sc.
- August 18th.—“ The Erect Posture : the Fight against Gravity ”, by Professor Harvey Sutton, O.B.E., M.D., D.P.H., B.Sc.
- September 15th.—“ Animals and Human Health ”, by Dudley A. Gill, M.R.C.V.S., D.V.S.M.
- October 20th.—“ Variable Stars ”, by the Rev. W. J. O’Leary, S.J.

The Annual Dinner was held on March 23rd at Farmer and Company’s Restaurant Annexe. The Society was honoured by the presence of His Excellency the Governor, the Lord Wakehurst, and the Attorney-General of New South Wales, the Honourable Sir Henry Manning, and eighty-seven persons were present.

The Walter Burfitt Prize for original research carried out during the three years ended December 31st, 1937, was awarded to Dr. F. M. Burnet, of the Walter and Eliza Hall Institute, Melbourne.

Alteration of Rules.—In accordance with a resolution passed on 30th October, 1935, the consequent alterations in the Rules were made effective by a motion substituting “ April ” for “ May ” in Rules IV, XIV, XXVI and XXXVIII, and by a motion substituting “ 30th April ” for “ 31st May ” in Rule XVII.

Government Grant.—During 1938 the Government grant received by the Royal Society was restored to the amount of £400 per annum.

Science House.—Meetings of the Science House Management Committee have been held regularly as usual. The Royal Society has been represented on the committee by Messrs. E. Cheel and A. R. Penfold, while Mr. M. B. Welch was appointed substitute member.

The financial position has improved owing to additional rooms and suites of rooms having been let during the year. There has been a consistent demand for the halls for meetings, and it is becoming necessary to book a considerable time in advance owing to that demand.

The arrears of subscriptions have been further reduced, an amount of £107 6s. in arrears having been collected during the year.

The Library.

The Council reappointed as Honorary Librarians for the year 1938-39 Professor J. C. Earl and Mr. H. Williams, and they, together with the Executive Committee, were elected as the Library Committee.

Purchase of Periodicals.—The amount of £33 18s. 4d. has been expended on periodicals during the past year.

Binding.—A considerable number of parts have been bound, at a cost of £30 6s. 6d.

The total expenditure on purchase and binding of books and periodicals is thus £64 4s. 10d.

Additional Shelving.—Additional shelving at a cost of £17 18s. 10d. was obtained during the year for the purpose of more adequately displaying the current periodicals. These shelves have now been placed in position, and add to the convenience of readers and also to the appearance of the library.

Exchanges and Accessions.—The total number of exchanges is 386.

For the twelve months ended February 28th, 1939, the number of accessions entered in the catalogue is 3,317 parts of periodicals and 297 whole volumes.

Borrowers and Readers.—The number of readers' tickets issued to the Australian Chemical Institute has been reduced to twenty-five, and the amount paid to £5 a year.

The number of readers who visited the library during the year has been 16, while the number of books and periodicals borrowed by members, accredited readers and institutions has been 85. Among the institutions which have availed themselves of the facilities offered by the Society's library are the Australian Museum, the Department of Works and Local Government, the University of Sydney, the MacMaster Laboratory of the University, the Metropolitan Water, Sewerage and Drainage Board, the Irrigation Commission, Amalgamated Wireless, the University of Tasmania, and the Division of Plant Industry, C.S.I.R., Canberra.

Gifts.—Mr. Andrew James Dixon presented a number of valuable books on mining and metallurgy to the library.

Hon. Librarian's Resignation.—The Hon. Librarian, Mr. H. Williams, tendered his resignation on account of his approaching departure for England, and recommended the appointment of an honorary librarian in his place at an early date, in order that he might give any possible assistance while still in Sydney.

Sale of Medical and other Books by Mr. Tyrrell.—Mr. Williams reported that owing to ill health he had not been able to carry very far his intentions with regard to the disposal of medical and other books, including duplicates, but recommended that this matter be attended to by the new librarian. He reported that Mr. Tyrrell was anxious that the matter should be proceeded with.

Storeroom.—The Honorary Librarians again drew attention to the condition of the Storeroom, on which they reported as follows at the end of 1936 :

“ The Storeroom is in a very unsatisfactory state, the stocks of the Society's *Journal and Proceedings* being kept in packing cases, from which it is difficult to get the Journals when they are required. Shelving 12 in. deep, which would hold a double row of volumes, could be fitted to the west wall of the storeroom, and should hold all or nearly all, of the Journals at present in the packing cases. Steel shelving, 10 ft. high, of ten bags, would cost about £41 11s.”

J. C. EARL,
President.

The following donations were received: 1,092 parts of periodicals and 63 whole volumes.

The President announced that the Clarke Memorial Medal for 1939 had been awarded to Mr. C. A. Sussmilch, and presented the medal to Mr. Sussmilch, who thanked the Council for the honour they had done him.

The President reported briefly on work done by the recently appointed National Emergency Committee.

The President, Professor J. C. Earl, delivered his address, entitled "The Use and Misuse of Science".

Professor J. C. Earl, the retiring President, then installed Dr. H. S. Halcro Wardlaw as President for the year 1939-1940, and the latter expressed his thanks. Professor Vonwiller expressed appreciation on behalf of the members to the retiring President for his work and for his address, and Professor Earl briefly replied.

The following papers were taken as read:

"Morpholinomethyl Alkyl Ethers", by Miss R. H. Harradence, M.Sc., and F. Lions, B.Sc., Ph.D.

"Researches on Indoles, Part IX, The Reaction of Phenylhydrazine with 'Mannich' Bases", by Miss R. H. Harradence, M.Sc., and F. Lions, B.Sc., Ph.D.

May 3, 1939.

The five hundred and sixty-eighth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

Dr. H. S. Halcro Wardlaw, 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 deaths of the following members, which had occurred since the December meeting: John Lane Mullins, a member since 1879; Samuel Cornwell, a member since 1882; Walter Blaxland, a member since 1888; Percy Moore Wood, a member since 1891; Fred Walsh, a member since 1906; Lindsay Duncan Cameron, a member since 1923; and the Rev. Father W. J. O'Leary, a member since 1930.

The certificates of three candidates for admission as ordinary members of the Society were read for the first time.

The following donations were received: 310 parts of periodicals and 17 whole numbers.

The following paper was read :

“The Mesozoic Stratigraphy of the Merriwa-Murrurundi District, and South-eastern Liverpool Plains”, by J. A. Dulhunty, B.Sc.

A lecturette illustrated by lantern slides, and entitled “Experiences in the U.S.A. and Great Britain”, was given by Mr. D. P. Mellor.

June 7, 1939.

The five hundred and sixty-ninth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

Dr. H. S. Halero Wardlaw, President, was in the chair. Twenty-two members and seven 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 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 : Elizabeth Marie Basnett, Ernest Ritchie, and Allan Maccoll.

Frederick Chapman, of Victoria, was elected an Honorary Member of the Society, in recognition of his research work in geology and palæontology extending over many years.

The following donations were received : 252 parts of periodicals and 80 whole numbers.

The following papers were read :

“The Reaction of 3, 5-Dinitrobenzoic Acid with Alkali. Part II, The main product of the Reaction of 3, 3'-dinitro-5, 5'-dicarboxyazoxybenzene”, by A. Bolliger, Ph.D., A.A.C.I., and F. Reuter, Ph.D., A.A.C.I.

“Refractive Index Determinations in the Infra-red for Parallel-sided Specimens of Glass”, by N. R. Hansen, B.Sc.

An address on “Biological Corrosion of Gas Mains” was given by Mr. E. G. Pont.

Professor Vonwiller showed and described lantern slides of photographs of emission spectra of metals and compounds.

An exhibit of a photo-electric colorimeter was made by Dr. A. Bolliger.

July 5, 1939.

The five hundred and seventieth General Monthly Meeting was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

Dr. H. S. Halcro Wardlaw, President, was in the chair. Twenty-four members and four visitors were present. The minutes of the preceding meeting were read and confirmed.

The certificate of one candidate for admission as an ordinary member was read for the first time.

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 : George Gascoigne Blake, Richard Charles Leslie Bosworth, and Norman Augustus Faull.

The following donations were received : 257 parts of periodicals and 19 whole numbers.

The following papers were read :

“The Age of the Marulan Batholith”, by G. F. K. Naylor, M.A., M.Sc.

“Studies in Metamorphism and Assimilation in the Cooma District of New South Wales. Part I. The Amphibolites and their Metasomatism”, by Germaine A. Joplin, B.Sc., Ph.D.

“The Construction of a Quartic Surface with Two Double Lines and Four Tropes”, by L. S. Goddard, B.Sc. (Communicated by Professor T. G. Room.)

“Infra-red Radiations with special Reference to their Quenching Effects upon Zinc Sulphide Phosphors”, by G. G. Blake, M.I.E.E., F.Inst.P.

An exhibit of Black Lamps was explained by Mr. D. P. Mellor.

August 2, 1939.

The five hundred and seventy-first General Monthly Meeting was held in the Hall of Science House, Gloucester Street, at 7.45 p.m.

The President, Dr. H. S. Halcro Wardlaw, was in the chair. The minutes of the preceding meeting were read and confirmed.

Nineteen members and one visitor were present.

The President announced the deaths of His Honour Judge A. P. Backhouse, the oldest member of the Society, elected in 1878, and Mr. Walter W. L'Estrange, a member since 1916.

The following donations were received : 266 parts of periodicals and 15 whole numbers.

The following papers were read :

- “ A Contribution to the Stereochemistry of Tervalent Nitrogen ”,
by F. Lions, B.Sc., Ph.D., A.I.C., and Ernest Ritchie.
- “ The Mesozoic Stratigraphy of the Gulgong-Coolah District ”,
by J. A. Dulhunty, B.Sc.

A lecturette on “ Distribution of Oil Supplies ” was delivered by Dr. H. G. Raggatt.

September 6, 1939.

The five hundred and seventy-second General Monthly Meeting was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

The President, Dr. H. S. Halero Wardlaw, was in the chair. The minutes of the preceding meeting were read and confirmed. Twenty-one members and five visitors were present.

The President announced the death of Wilfred Joseph Spruson, a member since 1917.

The certificate of one member for admission as an ordinary member was read for the second time, and Arthur James Lambeth was duly elected an ordinary member of the Society.

The following donations were received : 263 parts of periodicals and 22 whole numbers.

A lecturette was given by Mr. A. S. Le Souef, on “ The Coloration of Animals ”, illustrated with lantern slides and specimens.

A short talk was given by Mr. E. C. Andrews, on “ The Sixth Pacific Science Congress ”.

October 4, 1939.

The five hundred and seventy-third General Monthly Meeting was held in the Hall of Science House, Gloucester Street, Sydney, at 7.45 p.m.

Dr. H. S. Halero Wardlaw, President, was in the chair. The minutes of the preceding meeting were read and confirmed. Thirty members and three visitors were present.

The President announced the death of Harvey Nickoll, a member since 1924.

The certificate of one member for admission as an ordinary member of the Society was read for the first time.

The following donations were received : 196 parts of periodicals and nine whole numbers. A gift of a bound volume of early pamphlets on electricity was also received.

The following paper was read :

“Studies in Assimilation in the Wellington District. I. Hybridisation in the Wuuluman Creek Intrusion”, by Miss E. M. Basnett, B.Sc.

A lecturette on “Artificial Radio Activity” was given by Dr. F. L. Arnot.

November 1, 1939.

The five hundred and seventy-fourth General Monthly Meeting of the Society was held in the Hall of Science House, 157 Gloucester Street, Sydney, at 7.45 p.m.

Dr. H. S. Halcro Wardlaw, President, was in the chair. The minutes of the preceding meeting were read and confirmed. Twenty-five members and four visitors were present.

The certificate of one member for admission as an ordinary member of the Society was read for the first time.

The certificate of one member for admission as an ordinary member of the Society was read for the second time, and Alice Victoria May Thomas was duly elected as an ordinary member of the Society.

The following donations were received: 195 parts of periodicals and 17 whole numbers. 91 back numbers were also received.

The following paper was read :

“Infra-red Radiations and their Quenching Effect on Zinc Sulphide Phosphors”, by G. G. Blake, M.I.E.E., F.Inst.P.

A lecturette was given by Dr. W. E. H. Stanner on “An Expedition amongst the Natives of Central and East Africa”.

December 6, 1939.

The five hundred and seventy-fifth General Monthly Meeting of the Society was held in the Hall of Science House, 157 Gloucester Street, Sydney, at 7.45 p.m.

Dr. H. S. Halcro Wardlaw, President, was in the chair. The minutes of the preceding meeting were read and confirmed. Twenty-three members and one visitor were present.

The certificate of one candidate for admission as an ordinary member was read for the first time.

The certificate of one candidate for admission as an ordinary member of the Society was read for the second

time, and Robert Mortimer Gascoigne was duly elected as an ordinary member of the Society.

The following donations were received: 189 parts of periodicals and nine whole numbers.

The following papers were read:

- “The Triassic Fishes of Gosford, N.S.W. ”, by R. T. Wade, M.A., Ph.D. (Communicated by Dr. C. Anderson.)
 - “The Action of Progesterone on the Pouch of the Marsupial *Trichosurus vulpecula* ”, by A. Bolliger, Ph.D., and A. Carrodus, M.B., B.S.
 - “The Effect of Œstrogens on the Pouch of the Marsupial *Trichosurus vulpecula* ”, by A. Bolliger, Ph.D., and A. Carrodus, M.B., B.S.
 - “Magnetic Studies of Co-ordination Compounds. Part I., Cobaltous Compounds ”, by D. P. Mellor, M.Sc., and R. J. Goldacre, B.Sc.
 - “A Synthesis of Octahydropyrrocolines ”, by F. Lions, B.Sc., Ph.D., and A. M. Willison.
 - “4:5-Ethylene-iso-Quinoline Derivatives ”, by A. Flack, B.Sc., and F. Lions, B.Sc., Ph.D.
 - “Derivatives of 4-Hydroxy-Quinoline. Part II ”, by R. Gillis, F. Lions, B.Sc., Ph.D., and E. Ritchie, B.Sc.
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ABSTRACT OF PROCEEDINGS
OF THE SECTION OF
GEOLOGY

Chairman : Dr. A. B. Walkom.

Honorary Secretary : Mr. R. O. Chalmers.

Nine meetings were held during the year, and an average attendance of 11 members and nine visitors was maintained.

1939.

February 17.—Address by Sir John Flett, K.B.E., M.A., D.Sc., F.R.S., “British and Foreign Geological Surveys”.

April 21.—Exhibits : By Mr. L. L. Waterhouse : (a) Samarskite ; (b) Quartz in a conglomerate phase of the Hawkesbury Sandstone, from a quarry near Govett’s Leap, Blue Mountains. By Dr. Germaine A. Joplin : Cordierite-anthophyllite hornfels from Cornwall, Finland and Havilah, N. S. Wales. By Dr. Ida A. Brown : (a) Typical specimen of *Mucophyllum crateroides*, for comparison with recently collected material resembling *Mucophyllum* but showing six or seven buds with well developed tabulæ on the upper surface. This suggests that *Mucophyllum crateroides* is probably a form of *Tryplasma* like *Tryplasma liliiformis* Eth. fil. ; (b) *Martiniopsis subpentagonalis*, from the Salt Range, India ; *M. uralica*, from Bashkiria, U.S.S.R., and plaster casts of the holotypes of *M. subpentagonalis* and *M. inflata*, which all differ in their essential characters from any brachiopods known from the Upper Palæozoic of eastern Australia. This suggests that the genus *Martiniopsis* does not occur here. By Dr. F. A. Wiesener : (a) Banket ore from the Rand, South Africa, depth 8,500 feet ; (b) Natrolite from Victoria Falls ; (c) Granite used as a building stone in Moscow. By Mr. R. O. Chalmers : Latite from the Five Islands, Port Kembla, N. S. Wales. By Dr. A. B. Walkom : A small polished section of the Henbury meteoric iron.

May 19.—Address by Dr. Ida A. Brown, “Some Methods of Palæontological Research in England and North America”.

June 16.—Address by Mr. G. F. K. Naylor, “The General Geology of the Goulburn District, N. S. Wales”. Exhibits : By Mr. Naylor : (a) Concretions and probable plant remains from the Ryde Council’s quarry ; (b) A set of standardised colours drawn up by the Standards Association to denote types of rock, not geological formations.

July 21.—Address by Assistant Professor W. R. Browne, "Reflections on the Cainozoic History of Eastern New South Wales". Exhibits: By Dr. H. G. Raggatt: (a) Graptolites from 46 miles north-west of Condobolin, N. S. Wales, representing an extension of the Ordovician to the north of the Lachlan; (b) A twisted bore-core. By Professor L. A. Cotton: Concretionary structure and banding in crystalline gypsum from near Menindie, N. S. Wales.

August 11.—Exhibits: By Professor L. A. Cotton: (a) Plant remains in the Narrabeen sandstone; (b) Ellipsoidal sheared concretionary masses in Wianamatta shale, from the Burwood brick pit; (c) Horn-like masses of brassy-yellow gold, from the Bismarek Range, New Guinea. By Dr. A. B. Walkom: Specimens of *Rhacopteris* and *Glossopteris*, from Argentina. By Dr. H. G. Raggatt: Various surveying instruments to illustrate modern geological survey methods.

September 9.—Address by Mr. E. C. Andrews, "The Sixth Pacific Science Congress".

October 20.—Address by Mr. H. O. Fletcher, "The Simpson Desert". Exhibits: By Mr. Lambeth: Small pebbles of porphyry completely enclosed by a secondary deposit of calcite. By Mr. J. A. Dulhunty: A glaciated and striated pebble from the Triassic of Sandy Hollow in the Goulburn Valley, N. S. Wales.

November 17.—Address by Mr. J. A. Dulhunty, "The Mesozoic Stratigraphy and Structures of the Dubbo-Quirindi District, N. S. Wales". Exhibits: By Dr. Germaine A. Joplin: Apophyllite and lilac-coloured aragonite, from Prospect, N. S. Wales. By Dr. Ida A. Brown: Blastoid plates found in railway cutting, west of Branxton, N. S. Wales.

ABSTRACT OF PROCEEDINGS
OF THE SECTION OF
INDUSTRY

Chairman: A. D. Ollé, F.C.S., A.A.C.I.

The only visit made by members of the Section of Industry during the past year was to the McGarvie Smith Animal Husbandry Farm, Badgery's Creek. This was a particularly interesting excursion, and was well attended by members.

ABSTRACT OF PROCEEDINGS
OF THE SECTION OF
PHYSICAL SCIENCE

Chairman : Professor V. A. Bailey, M.A., D.Phil. (Oxon.)

Secretary : N. A. Faull, B.Sc.

Assistant Secretary : Miss J. Freeman.

Committee : Professor O. U. Vonwiller, Professor J. P. V. Madsen, Dr. W. H. Love, Dr. R. E. B. Makinson.

1939.

- April 5.—Dr. R. E. B. Makinson, "Work in Progress at the Cavendish Laboratory, Cambridge".
- May 10.—Election of Officers. Mr. N. F. Roberts, "Stable Frequency Division, using Selective Feed-back Circuits".
- June 7.—Mr. G. G. Blake, "Infra-red Radiation, with Special Reference to the Quenching of ZnS Phosphors".
- July 5.—Dr. S. E. Williams, "Nuclear Disintegration, and the Production of Energy in Stars".
- August 2.—"Transmission through and Reflection from Plates of Partially Absorbent Materials". Mr. T. Tasker, "Visible and Ultra-violet". Mr. N. Hansen, "Infra-red".
- August 16.—Mr. V. D. Burgmann, "A Multi-Circuit Electronic Relay Switch".
- September 23.—Dr. R. E. B. Makinson, "The Theory of Ferromagnetism".
- October 4.—Mr. W. B. Smith-White, "The Prime Number Theorem and Allied Theorems".
- November 1.—Professor V. A. Bailey and Miss Freeman, "The Generation of Artificial Auroras".
- November 22.—Dr. F. L. Arnot, "The Formation of Negative Ions and Molecules".
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The meetings listed above were the 130th to the 139th General Meetings of the Section of Physical Science.

The average attendance at the meetings was twenty-four (24) members and friends.

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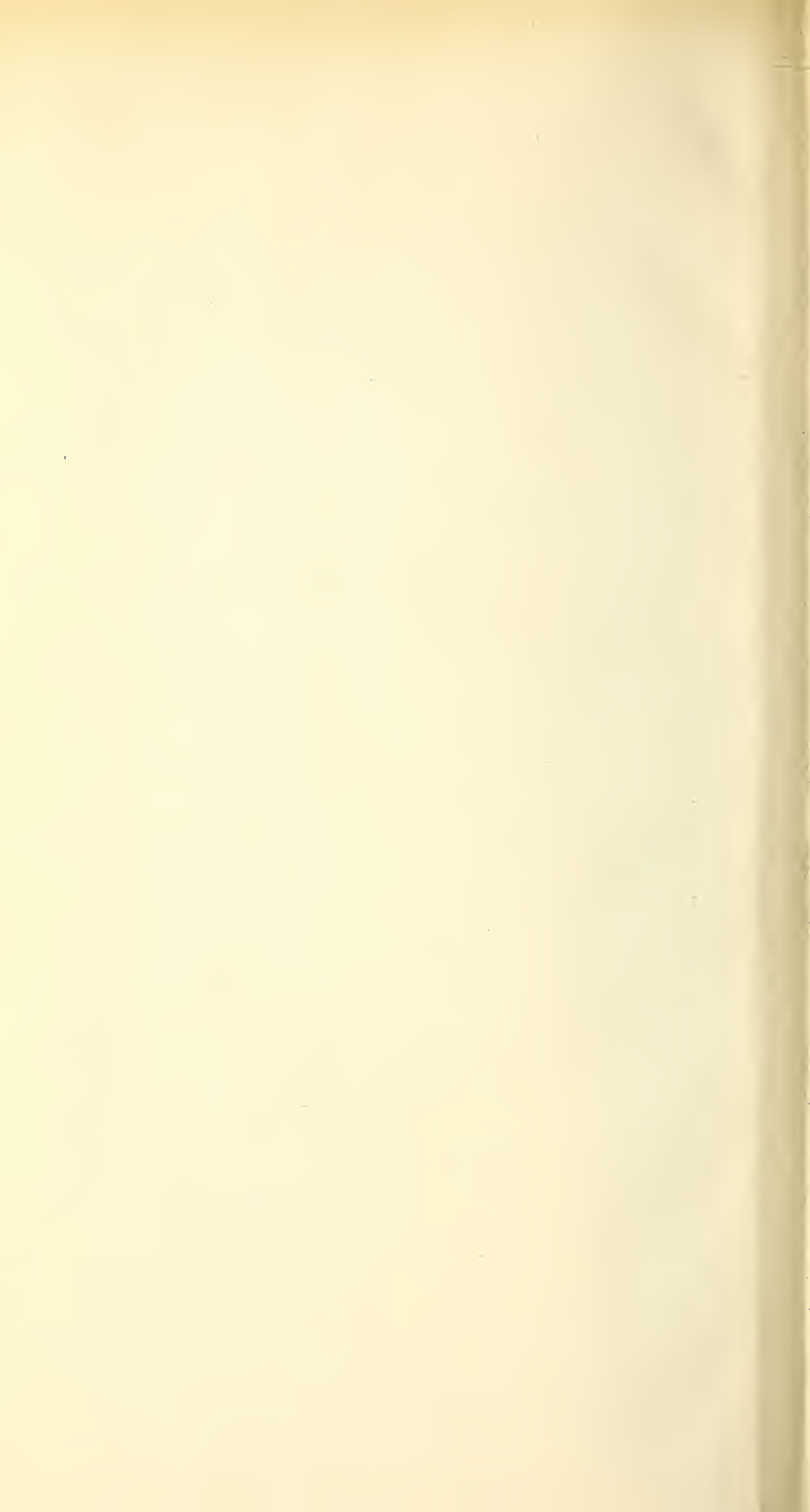
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