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FEBRUARY 1968

PROCEEDINGS
of the
1967 CONFERENCE
on
CITRUS CHEMISTRY
AND UTILIZATION

U. S. DEPT. OF AGRICULTURE
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Held at
Winter Haven, Fla.
October 13, 1967

Agricultural Research Service
United States Department of Agriculture

FOREWORD

This Conference is sponsored annually by the Southern Utilization Research and Development Division of the Agricultural Research Service, USDA. Its purpose is to report research developments in the area of citrus processing and utilization and to provide for an exchange of information that will benefit the industry and future research.

This Conference was held October 13, 1967, in Winter Haven, Fla., with V. C. Praschan, Fruit and Vegetable Products Laboratory, National Dairy Products Corporation, Glenview, Ill., serving as General Chairman. The program was developed by B. H. Wojcik, Assistant Director, under the guidance of C. H. Fisher, Director, (SURDD) in cooperation with staff members, and advisers representing the citrus industry.

This report summarizes the statements of the various speakers during the Conference, and gives an account of the discussions that followed. If further details are desired regarding any subject presented here, they may be obtained by communicating with the author concerned.

Underscored numbers in parentheses refer to references or literature cited at the end of the article. The figures, references, and tables are reproduced essentially as they were supplied by the writer of each paper.

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PROCEEDINGS OF THE 1967 CONFERENCE ON CITRUS CHEMISTRY AND UTILIZATION HELD AT WINTER HAVEN, FLA., OCTOBER 13, 1967

V. C. Praschan, General Chairman

Dr. Praschan, General Chairman, called the conference to order and introduced Dr. C. H.

Fisher who, on behalf of the Agricultural Research Service, welcomed those in attendance.

SESSION I: H. E. (Bert) Schulz, Chairman

ANALYSES OF STORED FOAM-MAT ORANGE AND GRAPEFRUIT CRYSTALS AND OF MODEL SYSTEMS

by

P. E. Shaw, J. H. Tatum, and R. E. Berry
Southern Utilization Research and Development Division
Fruit and Vegetable Products Laboratory
Winter Haven, Fla.

(Presented by P. E. Shaw)

Foam-mat dried orange and grapefruit crystals undergo nonenzymic browning upon prolonged storage at elevated temperatures. Generally, when stored under identical conditions, orange is first to develop a detectable flavor change. Orange and grapefruit were analyzed when a flavor change could first be detected by an experienced taste panel. In both samples, the same storage products were present in about the same quantities.

In studies of isolation of nonenzymic products formed during storage, 18 compounds have been identified thus far. Table 1 lists these as well as the compound believed from model studies to be the precursor for some of these storage products.

In addition to the fructose-acid model system reported on at last year's Citrus Conference, both a fructose-base model system and an ascorbic acid model system have been studied for further insight into the source and mechanisms of formation of storage products. Of special interest from the fructose-base degradation model system was the presence in the product mixture of compound 18 (table 1). This substance is a flavor component of pineapple concentrate and it has a sweet caramellike odor.

A qualitative estimate of nonenzymic browning in citrus crystals by observation of hydroxymethylfurfural (HMF) on thin-layer chromatography was developed in earlier work. However, a quantitative

Table 1. --Storage products from orange and grapefruit crystals

Compound	Precursor	
	Fructose	Ascorbic acid
1. Acetic acid	x	x
2. Furfural	x	x
3. 2-Acetylfuran		
4. 4-Hydroxy-2,3,5-hexanetrione	x	
5. 5-Methylfurfural	x	
6. n-Ethylpyrrole-2-carboxaldehyde		
7. γ -Butyrolactone		x
8. Furfuryl alcohol		x
9. Methylcyclopent-2-en-1-one		x
10. Tiglic acid		
11. 2-Acetylpyrrole		
12. 2-Hydroxyacetylfuran	x	x
13. 5-Methylpyrrole-2-carboxaldehyde		
14. 4-Hydroxy-2-hydroxy-3-methyl-5-methyl-3(2H)-furanone	x	
15. Levulinic acid	x	
16. Benzoic acid	x	
17. Hydroxymethylfurfural	x	
18. 2,5-Dimethyl-4-hydroxy-3(2H)-furanone	x (tentative)	

determination was desired. An experimental procedure involving (1) extraction of the stored citrus crystals and (2) the separation

of HMF by preparative thin-layer chromatography of the extract has given a value of 8 p. p. m. HMF in orange powder, which has just reached the point of detectable flavor change. This procedure assumes quantitative extraction and recovery of HMF upon preparative thin-layer chromatography, and thus it gives a minimum value only.

As a sideline, it appeared possible that the HMF method might be used as an indication of quality or heat damage in chilled juices, and exploratory experiments were conducted. Filtration of chilled juice through Filter-cel and ultraviolet measurements on the filtrate gave a broad maximum at 260 to 280 $m\mu$, which increased with increasing heat treatment for chilled juice in a given lot. This ultraviolet absorption was in the region expected for HMF. No correlation was found between ultraviolet absorption intensity and taste quality of samples from different lots. That is, the better-tasting juice sometimes had a stronger ultraviolet absorption, and no definite relationship could be established.

DISCUSSION

Question: Have you tried the hydroxymethylfurfural method on pasteurized chilled juice or canned juice?

P. E. Shaw: No, we have not.

Question: Do you think you would get the same pattern on chilled juice or canned juice that has been heated as you get from these powdered juices?

P. E. Shaw: I think we would, but I do not know whether or not this would be a quantitative measure.

Question: We appreciate your work on powders, but we desperately need this information on chilled juice. We need to know whether or not such a test would indicate the amount of heat treatment during pasteurization or adverse storage during distribution or not.

P. E. Shaw: We realize that this is needed and this will be tried shortly.

Question: Can you comment on time, moisture, and oxygen for the browning you mentioned?

P. E. Shaw: In a powder of 3-percent moisture, you would get more rapid browning than in one of 1-percent moisture. Oxygen does not seem to make a great deal of difference. It doesn't seem to make much difference whether or not the powder gets packaged under air or carbon dioxide.

Question: What about time?

P. E. Shaw: Well, for instance, the value I gave of 2.67 mg. is for powder that has been stored at 85° for 3 weeks, which was just at the point of off-flavor detectability by an experienced taste panel.

Question: Did you obtain any browning in those fructose solutions during 8 hours?

P. E. Shaw: No brown precipitate formed under our conditions, but there is a browning in a sense in that the solution becomes gradually darker and darker brown.

Question: Do you consider the reducing sugars to be the sole source of browning in these model systems?

P. E. Shaw: I do not consider it the sole source because ascorbic acid gave these products, and it is possible that even though the ascorbic acid is present in much smaller amounts, it is contributing to these products which are present in very small yield.

Question: Would a much more complex system that contains sugars, ascorbic acid, and amino acids be more equitable to solving this problem rather than a simple one containing largely the sugars in added solutions?

P. E. Shaw: The reason we took the acid sugar base system was primarily because of the simplicity of it. If you put in the amino acids, the browning rate is faster, but the compounds formed turn out to be the same--more or less. We have done some work with amino acids, but it does complicate the procedure, and we do not see a great difference in the products.

A PROCEDURE FOR OBTAINING RADIOACTIVE NARINGIN FROM GRAPEFRUIT LEAVES FED L-PHENYLALANINE-14C

by

J. F. Fisher

Southern Utilization Research and Development Division
Fruit and Vegetable Products Laboratory
Winter Haven, Fla.

(Presented by M. K. Veldhuis)

In recent years progress has been made in debittering grapefruit by removing the most prevalent bitter constituent naringin from the commercial product by various means. A different approach to the problem is to prevent the bitter constituents from being biosynthesized in the plant. To this end an investigation was undertaken to study the biogenesis of naringin and its tasteless isomer, naringenin-7 β -rutinoside.

The use of radioisotopes to label a compound allows one to follow a certain compound in its normal metabolic pathways in a living system and thus offer a possible clue as to where one can disrupt this normal biogeneric pathway and prevent the synthesis of the compound in question. To this end attempts were made to find a precursor to the biosynthesis of naringin. C¹⁴-carbon dioxide was readily photosynthesized into naringin. However, since incorporation of CO₂ is so general in the plant system, CO₂ did not readily offer us a tool in understanding the biogeneric pathway of naringin. Phenylalanine has been reported to be a precursor to flavonoids in buckwheat; and since biogeneric pathways generally are not specific to one species, phenylalanine was a most likely candidate as a precursor to the flavonoid naringin. When young grapefruit leaves were fed L-phenylalanine-14C, radioactive naringin (naringenin-7 β -neohesperidoside) and naringenin-7 β -rutinoside were isolated.

The method employs radiolabeled L-phenylalanine, which is taken up by young grapefruit leaves through the petioles. The leaves are then allowed to metabolize the

phenylalanine during periods of 12 hours of light and 12 hours of dark. Extraction of the leaves with hot methyl alcohol, followed by concentration and column chromatography, afforded both the bitter naringin and its tasteless isomer. Final separation and purification of both compounds were accomplished by thin-layer chromatography. The availability of these radiolabeled compounds will enable us to advance our knowledge concerning the site of synthesis and translocation of naringin as well as its biosynthesis and metabolism in the grapefruit plant. The availability of radiolabeled naringin allows chemists to synthesize labeled derivatives of naringin such as the dihydrochalcone, a possible sugar substitute, for further tracer research. Another possible use for these compounds is in analytical methods for naringin in which a certain amount of the labeled naringin, would be added to a sample, mixed, and a small amount of pure naringin recovered. From the radioactivity of the sample recovered and the amount of radioactive naringin added, the amount of original naringin could be calculated. This procedure would be applicable to very small samples.

DISCUSSION

Question: Did you do a material balance on the conversion of phenylalanine to the naringin compounds?

M. K. Veldhuis: No material balance was run, but most of the radioactivity in the end product was in the naringin and its tasteless isomer, so the yield should have been quite good.

BASIC STUDIES ON ENZYMES IN CITRUS PRODUCTS

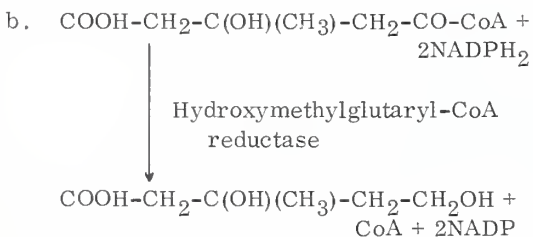
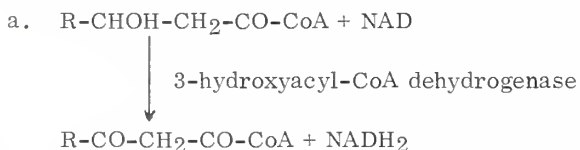
by

J. H. Bruemmer, R. A. Baker, and B. Roe
Southern Utilization Research and Development Division
Fruit and Vegetable Products Laboratory
Winter Haven, Fla.

(Presented by J. H. Bruemmer)

The purpose of these studies was to determine whether or not mature citrus fruit is capable of supporting the types of oxidation reduction reactions that are associated with biosynthetic processes in plant tissue. This information is essential to our recently initiated Enzyme Research Program in developing an experimental approach to select and study those reactions in the biosynthetic pathway of aliphatic and terpenoid oxygenated compounds that can be controlled during processing of citrus so as to enhance the flavor of fruit and juice products.

The type reaction under investigation requires the coenzyme, nicotinamide adenine dinucleotide (NAD), or its phosphate (NADP). This type of reaction accounts for most of the known oxidations and reductions that occur in the various reaction pathways of plant tissue metabolism. The coenzyme functions as the electron acceptor during the oxidation of a compound as in the degradative pathway of fatty acid (fig. 1a) and as the donor in the reduction reaction as in the biosynthetic pathway to the terpenoids (fig. 1b).



CoA stands for Coenzyme A: 3'phospho-adenosine diphosphate-pentoyl-β-alanyl-cysteamine.

The coenzyme is loosely bound to the enzyme so that the same coenzyme molecule can serve first as a reductant for one reaction and then as an oxidant for a second reaction. This versatility enables the coenzyme to function as an effective regulator of a series of metabolic reactions.

We examined extracts of juice sacs from mature oranges and grapefruit to determine the distribution of the coenzymes in their reduced and oxidized forms.

The results of our analyses are shown in table 1. NADP was present mostly as the reduced form, whereas the oxidized form of NAD was predominant in both fruits.

Assuming that all of the NADP is available for enzyme reactions, then these results indicate that more than one-half is available for the reductase reactions and suggest that, in terms of coenzyme requirements, conditions in mature fruit are favorable for biosynthesis.

The low ratio of reduced to oxidized NAD suggests that mature fruit has a very active oxidase for $NADH_2$. Four terminal oxidases and corresponding coupling reductases that oxidize $NADH_2$ are known to occur in plant tissue. These are listed in figure 2. Since one or more of these systems might be the responsible oxidant, we examined particulate fractions from juice sacs of mature grapefruit and oranges for oxidase activity with $NADH_2$, cytochrome c, ascorbate, catechol, and glycollate.

Cytochrome c was the only substrate that was rapidly oxidized, although some activity was detected with ascorbate and catechol. Highest activity was observed in the particulate fraction that sedimented between 1,000 and 10,000 x G in 15 minutes. This fraction from the orange oxidized cytochrome c in terms of oxygen consumed at the rate of 14 microatoms of O_2 per hour per mg. protein

Figure 1.—Typical reactions requiring NAD and NADP

<u>Terminal Oxidase</u>	<u>Coupling Reductase</u>
Cytochrome c oxidase	Cytochrome c reductase
Ascorbic acid oxidase	Dehydroascorbic acid and glutathione reductase
Phenol oxidase	Quinone reductase
Glycollic acid oxidase	Glyoxylic acid reductase

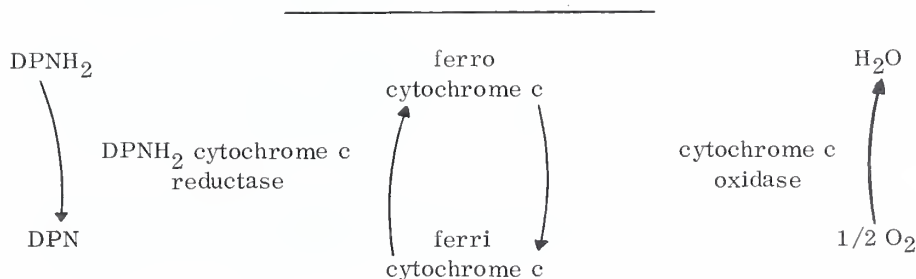


Figure 2. --Coupling of NADH₂ oxidation to terminal oxidase.

Table 1. --Concentration of pyridine nucleotide coenzymes in juice sacs from mature oranges and grapefruit^{1/}

FRUIT	NADPH ₂	NADP	$\frac{\text{NADPH}_2}{\text{NADP}}$	NADH ₂	NAD	$\frac{\text{NADH}_2}{\text{NAD}}$
Grapefruit	0.92	0.69	1.3	0.51	3.95	0.13
Oranges	1.22	0.93	1.3	1.65	7.86	0.21

^{1/} Each value represents concentration in micrograms per ml. juice and is the average of 10 samples.

in the fraction. The corresponding fraction from grapefruit was only about one-third as active.

The fraction with the highest cytochrome c oxidase activity also had the highest NADH₂-cytochrome c reductase activity. Expressed in terms of O₂ utilized, the rate of oxidation by the reductase was 5 microatome of O₂ per hour per mg. protein. The coupling of the reductase and the oxidase through cytochrome

c to form an NADH₂-oxidase is diagramed in figure 2.

These observations on the oxidation of NADH₂ indicate that mature grapefruit and oranges have an active NAD oxidase system and suggest that coupling the oxidation of NADH₂ through cytochrome c reductase to molecular O₂ probably serves as the energy generating system for biosynthetic reactions in citrus.

DISCUSSION

Question: Would the spraying of a fruit or leaf with ascorbic acid increase the reducing power of the sap or the enzyme systems?

J. H. Bruemmer: Well, I really can't say. To study this you would have to get the material into the plant. You will recall the difficulty people have been having in getting material into the plant and getting them to do the work desired. There is quite a bit of ascorbic acid in the fruit, but I do not know about the amounts present in the leaves or stems. It would probably be readily metabolized, if it weren't oxidized before it was absorbed.

Question: In your statements you indicated that you were working with mature fruit. Exactly what state do you mean?

J. H. Bruemmer: Let's say that they were very mature; that is, the grapefruit had a Brix/acid ratio of 10 to 1 and the Valencia orange a ratio of 20 to 1.

Question: Would these enzymes you are talking about be active in citrus juice crystals?

J. H. Bruemmer: Not under the conditions they use in making the crystals. Proteins are quite labile; the enzymes, themselves, are very labile and would have been destroyed under the acid conditions and heat.

CHEMICAL CHARACTERIZATION OF LEMON JUICE PRODUCTS

by

C. E. Vandercook

Western Utilization Research and Development Division

Fruit and Vegetable Chemistry Laboratory

Pasadena, Calif.

A large percentage of the U. S. lemon crop is processed into juice and juice products. These products are sold commercially on the basis of their acidity which is primarily citric acid. It is sometimes desirable to be able to characterize lemon juice in terms of constituents other than citric acid. In an attempt to achieve this goal, methods of analysis were adapted to lemon juice for the measurement of total acidity as citric acid, total amino acids by formol titration, 1-malic acid by optical rotation, and total phenolics by UV absorbance. Originally, 61 samples of California and Arizona lemon juice concentrates were analyzed for these constituents. The data were treated by a multiple regression approach. This yielded an equation whereby the citric acid content of a sample could be predicted on the basis of these other constituents. Confidence limits were set at the 99-percent level which gave a maximum citric acid difference of 19.1 meq./100 ml. This means that with natural juice, titrated citric acid values will be no more than 19.1 units away from the predicted values in 99 cases out of 100.

To further characterize lemon juice, the individual amino acids were chromato-

graphed on paper and passed through a recording densitometer. The pattern was fairly constant. Individual phenolics were also estimated by a paper chromatographic system and densitometer. The sum of the individual compounds closely followed the UV absorbance.

A method for the extraction and measurement of sterols and carotenoids was developed, and many lemon juice samples were tested. Correlation studies of the carotenoid and sterol values with the other constituents used in the multiple regression showed no significant improvement in the reliability of the equation with the additional analyses.

A study of the effects of fruit storage on the selected constituents showed that in one batch of lemons the 1-malic acid dropped 64 percent in 15 weeks. The amino acid concentration increased by 34 percent, while the total phenolics and citric acid remained constant. In spite of these changes, the citric acid value predicted by the multiple regression equation remained nearly constant.

The use of heavy extraction pressures by an FMC extractor, as compared with light pressures, produced a small increase in the total amino acids and total phenolics in the

extracted lemon juice. The other constituents were unchanged. Tighter juice finishing pressures had the effect of increasing the pectin content but not the other constituents. The relationship between the predicted and measured citric acid values was not greatly changed.

Bottled lemon juice intended for room temperature storage at the retail level is commonly treated with chemical preservatives to prevent deterioration. A study of the effects of sulfur dioxide, sodium benzoate, and potassium sorbate preservatives on the previously mentioned analytical methods confirmed that there is no initial effect caused by these preservatives (except for the formol determination of amino acids, in which case the added SO_2 had to be expelled by boiling 1 min.). On storage of the preserved juices at 5° to 35° C. for up to 17 weeks, small but statistically significant changes in composition were observed in some of the juice samples. For practical applications the changes did not affect the multiple regression approach.

There are a number of other factors that could conceivably influence the composition of the juice, such as variety, season, growing area, and cultural practices which have not yet been thoroughly investigated in this study. Furthermore, it would be impractical to even consider the many possible combinations of factors. However, the limited investigations into some of the important ones indicate that the multiple regression approach may be applied to chemically characterize any commercial lemon juice product.

DISCUSSION

Question: Have you tried any Meyer lemons?

C. E. Vandercook: We have looked at three or four samples of Meyer lemons. There are some differences, but those juice samples followed the general compositional pattern. We hope to get more samples from Florida.

Question: I notice you use four variables in your prediction equation; did all these four variables enter into it? Could we see the general formula of your prediction on equation?

C. E. Vandercook: The general prediction equation relates the amino acids, 1-malic acid and the phenolics to the citric acid content. The equation from our samples is that citrus acid equals $12.01 \times$ total amino acids plus $2.71 \times$ malic acid plus $30.06 \times$ total phenolics. On the basis of this equation the predicted values were close to the measured citric acid. We found that better than 99 percent of the samples examined had a predicted citric acid within 19.1 units of the measured citric acid. With a greater difference, the sample would be highly suspect.

Question: Have you tried to get a profile of the volatile components in lemon juice?

C. E. Vandercook: No. We felt that the other constituents--amino acids, malic acid, and total phenolics--which are present at a fairly high level would be a better index of citric acid. The volatile constituents could be added easily from lemon oil, and their level would be largely a function of processing.

Question: Why did you use 1-malic acid as the index instead of the group of acids?

C. E. Vandercook: We used 1-malic acid because the optically active isomer is too expensive to add to the juice. The malic acid was only one of three constituents used in the predicting citric acid. This avoided the dependence of any one constituent for the index.

WHAT IS A NATURAL FLAVOR?

by

S. R. Hoover

Nutrition, Consumer and Industrial Use Research
Washington, D. C.

Flavors come in various types and sizes. A few occur just as we savor them; citrus fruits are of this type. Others are produced enzymically when tissue is damaged--onions and garlic are the classical examples. Some are produced by fermentation. Processing steps

produce flavors--ham and corned beef illustrate these. Most of our foods derive their essential flavor from chemical reactions that occur during cooking. We have herbs and seasonings, monosodium glutamate, and now nucleotides. Which of these are natural flavors?

POTENTIAL UTILIZATION OF SOME CHEMICALS FROM CITRUS FRUIT

by

E. D. Lund

Southern Utilization Research and Development Division
Fruit and Vegetable Products Laboratory
Winter Haven, Fla.

A number of potential new chemical by-products from citrus have been proposed recently by members of the staff of the Fruit and Vegetable Products Laboratory. This paper will summarize these proposals with comments on the potential economic return to be expected. In some cases, the chemical reactions involved are somewhat speculative. However, the intent of this paper is only to suggest promising chemical routes to new products.

Peel Oil--d-Limonene, the major constituent of citrus peel oils, is currently available in 10- to 20-million-pound quantities annually at 10 to 15 cents per pound. It is presently used as a relatively high boiling organic solvent in a number of applications. The compound is very effective in penetrating grease. Its use as an automotive degreaser has been demonstrated by this laboratory. It is very effective as a solvent in other ways such as removing silicones and various types of organic residues from laboratory glassware, cleaning epoxy cement, etc. It may have possibilities as a gel or cr me-type hand cleaner if it can be shown that trouble from dermatitis is not encountered.

The preparation of limonene derivatives has been a subject of study for many years. Since the citrus byproduct limonene is a

single optical isomer, one would like to make use of this optical activity, especially since dipentene, the racemic mixture of d- and l-limonene, is competitive in price with d-limonene and could replace d-limonene for any use not involving optical activity.

The optically active ether derivatives dihydropinol (I), and the ethers (II) and (III) (figure 1), can be produced from d-limonene in good yield. They should be stable, except under strongly acidic conditions. The use of these ether derivatives as solvents, especially for reactions involving ether complexed intermediates could conceivably result in asymmetric synthesis.

The use of the optically active tertiary Grignard reagent (IV) (figure 1) for asymmetric reductions has been reported in the literature. In the particular example concerned, no asymmetric product was produced; however, this negative result is based on the reduction of only a single ketone. Further studies on the use of this asymmetric Grignard reagent with a variety of ketones should be undertaken in order to establish the true nature of its potential as an asymmetric reducing agent.

A recent paper has reported on the use of limonene as a hydrogen donor for the reduction of certain double bonds and nitro

groups in the presence of palladium catalyst. *p*-Cymene is the byproduct. It would be interesting to attempt an asymmetric reduction with this system using *d*-limonene as the hydrogen donor.

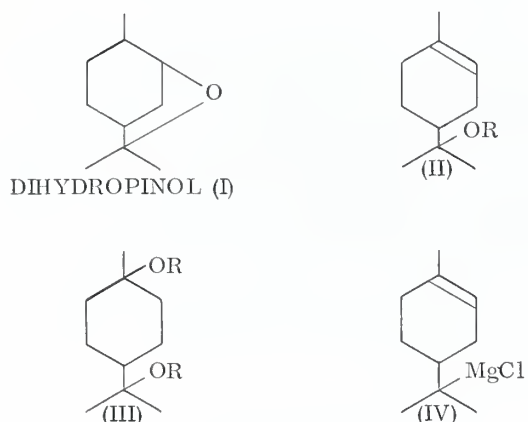


Figure 1

Piperitone and perillartine are related to limonene. Piperitone is used in perfumes and dentifrices to impart a minty flavor and has a current market price of about \$5 per pound. Perillartine is a synthetic sweetening agent used commercially in Japan. The use of limonene as a source for the above two compounds was proposed by Philip Shaw of the Fruit and Vegetable Products Laboratory.

Although the constituents of citrus oils other than limonene only account for 4 to 10 percent of the total, it might be profitable to utilize some of them commercially, provided that the separation from the oil was reasonably straightforward and assuming that the product is quite active or potent so that its value would be high.

Orange and lemon oils in undiluted form have been recently shown to be potent bacteriostats and fungistats. For example, a concentration of 2,000 p. p. m. of orange oil was shown to be as effective in inhibiting bacterial growth in foods as 10 p. p. m. of the antibiotic tylosin. The active ingredient is unknown. The flavonoid compounds, nobiletin and tangeretin, were shown in a recent article to have fungistatic activity against the fungi responsible for "Mal-Secco" disease of citrus in the Mediterranean area. Fungistatic effects of nobiletin have been

verified in another laboratory. The activity of these two compounds, as well as other citrus oil components, against various microorganisms should be tested, since there seem to be some highly active compounds present. Approximately 6,000 pounds each of nobiletin and tangeretin are available annually from orange and tangerine oil and can be readily separated from these oils.

Valencene is the major sesquiterpene present in orange oil. It can be separated from the oil by a fairly straightforward procedure. The total amount available annually is approximately 2,000 pounds. Valencene can be converted by one-step reaction to nookatone, the principal distinctive flavoring component of grapefruit. The related compound, α -vetivone, is one of the major constituents of vetiver oil, which is used in perfumes of an oriental nature. It should be possible to convert nookatone into α -vetivone by rearrangement of the double bond.

The coumarins, bergaptol and umbelliferone, can be isolated in fair quantities from certain citrus oils. The related compound, bergaptene, is active as a dermal photosensitizer and molluscicide, while visnadin is a vasodilator used in Europe for treatment of angina pectoris. The conversion of the coumarin raw materials to the active products can be accomplished with reasonably high yields.

Citrus Pulp. -- The pulp constitutes approximately 45 percent by weight of the citrus fruit. The flavonoid glycosides, hesperidin, naringin, and lemon bioflavonoid complex, containing substantial quantities of eriocitrin and diosmin are produced from the pulp as by-products of citrus processing. The estimated amounts available, based on production figures for the 1965-66 season, are tabulated below.

<u>Glycoside</u>	<u>Aglycone</u>	Available amount <u>Pound</u>
Naringin	Naringenin	810,000
Hesperidin	Hesperitin	3,200,000
Eriocitrin	Eriodictoyl	Approximately 100,000

The figures quoted are based on the aglycone. The current price for the glycosides ranges from \$5 to \$10 per pound.

The glycosides can be broken down to give phloroglucinol plus a substituted phenethylamine. If the stereochemistry at C-2 could be retained, the resultant phenethylamine derivative would be optically active. The current value of phloroglucinol is \$10 per pound, while the value of the phenethylamine derivative would vary from \$10 to \$500 per pound, depending on the particular type of phenethylamine derivative and the stereochemistry of the asymmetric center. Many of the substituted phenethylamines are used as sympathomimetic drugs and in some cases one optical isomer is considerably more active than the other. For example, (-) epinephrine is around twenty times as active as the (+) form and commands a correspondingly higher price. If the flavo-

noid could be degraded in a fairly straightforward manner so as to give phloroglucinol plus an optically active phenethylamine derivative, the process could represent an economically attractive outlet for flavonoid byproducts.

Although many of these substances are present in minor amounts in citrus, the enzymic reactions leading to their biosynthesis probably can be controlled to increase their normal concentration hundredfold to ten thousandfold. Temperature, pH, and environmental gas control, as well as specific inhibitors, can control the metabolic pathways in biological material. Selective use of these agents might make it possible to convert the excised fruit into a miniature fermenter for production of drugs.

SESSION II: C. R. Sutherland, Chairman

CITRUS WORK AT THE WESLACO LABORATORY

by

B. J. Lime, R. F. Albach, and F. I. Meredith
Southern Utilization Research and Development Division
Food Crops Utilization Research Laboratory
Weslaco, Tex.

(Presented by B. J. Lime)

Approximately two-thirds of the citrus production in Texas is red grapefruit. The major problems associated with processing this variety of fruit are centered around its color and bitterness.

An investigation of the occurrence of naringin in Texas red grapefruit has shown that radioactive $C^{14}O_2$ is fixed in the flavonoids only in the very early stages of fruit growth. Maximum fixation occurred on April 17, when the fruit was 16 mm. diameter and incorporation ceased after May 18, when the fruit was 37 mm. diameter. The total naringin content continued to increase and reached a maximum August 1, approximately 10 weeks after CO_2 fixation ceased to appear in the flavonoids. The study has also shown that fruit set early in the season contained 20 to 25 percent more naringin during the harvesting season than fruit set 4 months later.

Oil sprays used on Texas red grapefruit for citrus pest control had no significant effect on the color or bitterness of the fruit.

A new variety of red grapefruit ("Hudson") has shown excellent processing characteristics. By late March it was 50 percent larger than the Ruby Red with 2-1/2 times the lycopene content. The sugar and acid content is approximately the same as other varieties of Texas citrus.

DISCUSSION

Question: In Florida we centrifuge the mixture of juice, remove a considerable amount of pulp, and lower the naringin at the same time. You are trying to capitalize on this. Do you centrifuge your products?

B. J. Lime: No sir, we are trying to capitalize on the color by maintaining high pulp level

and industry in that area has decided that the thing to do is to keep the juice as pronounced red or pink as possible. Of course, our limiting factor in adding pulp is the bitterness and this is one of the reasons we have been interested in the bitterness problem.

Question: What effect did the hurricanes have on the grapefruit crop?

B. J. Lime: The USDA report reduces the grapefruit estimate from 6 to 1.7 million boxes. The guesses from industry vary widely. When I left, the average guess was around 2 million for grapefruit and for oranges around 1.5 million.

Question: Will they lose any trees?

B. J. Lime: They lost very few trees, and there was very little wood damage. There

was some defoliation, and this is one of the problems that the people there do not have the answer to. There is new growth coming on now. The question is: Will this new growth harden off and will it product fruit next year?

Question: You mentioned glycosides in early fruit, but how about late-bloom fruit? Have you checked that?

B. J. Lime: No, but we intend to. In fact, we are looking for off-bloom trees right now to continue this. This is one of the things we hope is a lead to this kind of situation. If it is a temperature cutoff, it would indicate that the later the fruit bloomed, possibly the lower the naringin, and we would hope that delaying the fruit set for a week or two might decrease naringin.

A REVIEW OF APPLIED RESEARCH ON FRUIT JUICE CRYSTALS

by

R. E. Berry, O. W. Bissett, C. J. Wagner, Jr., and J. L. Froscher
Southern Utilization Research and Development Division
Fruit and Vegetable Products Laboratory
Winter Haven, Fla.

(Presented by R. E. Berry)

The preparation of citrus juice crystals has been studied by using two different dehydration methods--freeze drying and foam-mat drying. When orange juice of 10° and 20° Brix was freeze dried using different sample forms, frozen juice ground into very fine particles appeared to dry best in a large pilot-scale freeze drier. Samples of about 20-mesh U. S. sieve size dried more rapidly and more thoroughly than a slab, and samples of about 60-mesh U. S. sieve size dried even more efficiently. A smaller scale freezer drier with greater potential for controlling variables has been received, and a more carefully controlled experiment is being undertaken at present to verify these findings.

In another study of freeze-dried citrus juices, samples of orange juice were prepared under standard conditions to determine the effects of initial adsorbed gas layer on stability of the product. There has been speculation that, with freeze-dried products,

the critical factor for storage might be the nature of the first gas to contact the dehydrated material, i. e., the gas with which the vacuum is broken. Samples of orange juice were prepared where the vacuum was broken with air, and these were compared to samples where the vacuum was broken with carbon dioxide. In each of these samples, further variables consisted of the packaging atmospheres--air or carbon dioxide. Storage is in progress.

A series of experiments was conducted to determine what foam-mat drying conditions might need to be adapted for changes in characteristics of the concentrate. Several experimental orange concentrates were prepared by using varying types of extraction, extraction pressures, and finishing techniques. These resulted in a number of concentrates containing differing amounts of oil, suspended solids, pulp content, and varying in viscosity. These juices were then concentrated, and the concentrates were foam-mat dried. No major

changes in foam-mat drying conditions were required for the different concentrates. The primary changes required were in foam-making techniques. For concentrates with lesser pulp content and lower viscosities, different foaming agents were required. In these cases, an algin derivative and a high viscosity methylcellulose, or carboxy-methylcellulose, were required in addition to the regular methylcellulose. There was very little difference in initial quality or storage stability of these experimental samples--all were about the same as standard foam-mat dried crystals.

Flavor evaluations were carried out on orange juice crystals prepared by foam-mat drying, used with different levels of "locked-in" oil. The evaluations were made in cooperation with the Statistical Reporting Service, U. S. Department of Agriculture, Washington, D. C. Untrained tasters preferred samples with increasing oil content up to 0.030 percent (g. oil/100 ml. juice). From 0.030 to 0.060 percent there was no significant difference in preference. With grapefruit juice, increasing levels of oil were preferred from 0.005 to 0.012 percent. Based on these studies, samples of orange and grapefruit crystals with higher oil content were prepared. Storage life of these samples was extended considerably over that found in previous studies. In another series of experiments, cold-pressed peel oil was added to the concentrate before drying, and the amount retained in the dried product was determined by the bromate titration method. Approximately 60 percent added oil was retained. There was little difference between the quality of these samples and conventional samples containing "locked-in" oil. The amount of oil retained after drying varied from 55 to 75 percent, depending upon the original level of oil and the drying conditions.

Sulfur dioxide was added in the form of sodium bisulfite to orange concentrate before drying. The amount of SO₂ was then determined in the final product on a basis of p. p. m. in reconstituted juice. Amounts varying from about 20 p. p. m. to about 200 p. p. m. SO₂ were used. There was some extension of storage time before a detectable difference occurred when higher levels of SO₂ were used. Levels of SO₂ from about 20 to about 100 p. p. m. had little effect.

Foam-mat drying has been extended to a number of subtropical and tropical fruits including guava, pineapple, and strawberry. Foaming conditions have been developed, and drying conditions have been studied. For these fruits, usually additional thickening agents, such as high viscosity methylcellulose or algin derivatives, were required. Products with good initial quality have been prepared, and storage stability of these is presently under study. These products have been blended with foam-mat dried orange and grapefruit juices to provide additional new fruit-drink products as well.

DISCUSSION

Question: Were there any unusual flavors brought about by the use of sulfur dioxide or carboxy-methylcellulose?

R. E. Berry: Sulfur dioxide gave no undesirable flavor at all that we could detect. Carboxy-methylcellulose, particularly in the higher amounts, gave an unusual mouth feel but no particular change in flavor.

Question: In one of your slides you showed that the quick fiber test was considerably lower and you had used an emulsifying agent. Is the quick fiber related to insoluble solids in the juice crystals?

R. E. Berry: The lower the quick fiber number, the harder the finish. That is, the drier the pulp. Generally speaking, this also means the more insoluble solids there will be in the juice.

Comment: I don't have a question, but I'd like to make some comments: I'd like to congratulate you on the broad approach you are taking covering the different aspects of dehydration. I'd also wish to congratulate your courage for including something other than citrus in your foam-mat drying. The third comment has to do with freeze-drying. I'd imagine that you are familiar with the continuous freeze-drying process using ultrasonic vibrations. Studies on it pretty well bear out what you are finding, with respect to the essential effect of particle size. Essentially the vibration constantly turns over the particles to expose increasingly greater surface to the heat source. In that system, drying times on the order of 45 minutes for

a thing like 40 to 20 percent coffee solids have been attained. This may have application here.

Question: You mention moisture levels of 1.1 to 1.2 percent; what is the relationship of storage life to moisture levels?

R. E. Berry: As indicated in a previous talk, as long as the moisture content is below 1.30 percent storage life is about the same for all samples. From 1.3 percent on up, the storage stability is shortened; that is, storage changes are hastened quite a bit by increasing the amount of moisture above the 1.3 percent level, lowering it below 1.3 percent had little effect.

PRINCIPLES OF MICROFLAKE FOOD DEHYDRATION

by
R. J. Moshy
American Machine and Foundry Co.
Springdale, Conn.

The Microflake Food Dehydration System (MFD) was designed to fill a gap in the spectrum of existing drying methods. It is an atmospheric, continuous belt-drying process for liquid food foams. In the later respect, i. e., food foams, it is akin to the USDA foam-mat process.

The dehydration is accomplished in approximately 60 seconds at a minimum product temperature of 170° F. This is accomplished by casting food foam in a layer of approximately 10 to 40 mills on a solid stainless steel belt, and heating from below by the direct condensation of steam, and from above by heated air. The product is doctored from the belt in the form of small, porous crystals.

The unique features of the MFD process reside in the engineering advances in the steam box dryer design, heated air system, foam generation, and precision in film casting, which makes the "low temperature, short-time" drying cycle possible at overall evaporation rates of 1 to 3 pounds of water removed per square foot of dryer surface per hour.

In addition, since the air chambers and steam boxes are divided into separate zones, the product temperature along the belt is precisely controlled. Further control of product temperature in the doctoring zone is used to modify the physical characteristics of the doctored product.

DISCUSSION

Question: You referred to bubble size. Do you refer to bubble size before or after the product is dried? When the bubbles hit the hot part of the belt, the bubble size should increase.

R. J. Moshy: There are two effects: One effect of foam collapse when the bubbles hit the heated section. Whether this is by exploding the foam or reduced surface tension due to the effect of the surface-active or emulsifying agents, I don't know. However, the effect is that we get foam collapse as I believe is the case in foam-mat drying. I imagine our effect is more drastic because we are in and out of the drying zone so rapidly. Then there is an effect of temperature on bubble size. Heating the underside of the belt causes the foam to set. If the foam doesn't set, you get boiling rather than evaporation. Voids will form and the foam will collapse, which results in a buildup of thermal resistance.

Question: Would you comment on cost?

R. J. Moshy: For a capacity of 2 million pounds a year of dry product with 50 percent overdesign, the capital cost is less than a half-million dollars, installed. Operating costs are less than 4 cents per pound water removed. Is that sufficient? We start running into trouble at low production volumes. It takes two men to run the dryer

regardless of whether the output is 5, 2, or 1 million pounds.

Question: What do you figure as a normal annual operating time?

R. J. Moshy: We figure on 24 hours a day, 250 days a year, or 6,000 hours a year with 10 percent down time so it would be operating 5,400 hours.

Question: What about losses?

R. J. Moshy: There are none. The only place for product loss is inefficiency in doctoring, that is, if you do not doctor cleanly. This is the only place you can lose product.

Question: It has to stick on the belt. You can't use a screen then, can you?

R. J. Moshy: No, you wouldn't get past the steam box since steam is impinged directly against the underside of the belt.

Question: What Brix do you start with on the drying?

R. J. Moshy: Typically, for orange juice we use 58° Brix concentrate. In case of tomatoes, it would range from 30 to 33 percent; molasses 72 percent; and milk 42 percent. We use as high concentration as we can.

A REVIEW OF CONSUMER RESEARCH ON CITRUS PRODUCTS

by
Margaret Weidenhamer
Special Surveys Branch
Standards and Research Division
Statistical Reporting Service, USDA
Washington, D. C.

About a year and a half ago, we began planning a household placement test for foam-mat dried grapefruit juice crystals from the Fruit and Vegetable Products Laboratory^{1/}, Winter Haven, Fla., in cooperation with Agricultural Research Service (ARS) and the Florida Citrus Commission.

The overall objective of the research was twofold: To evaluate consumer acceptance of foam-mat dried grapefruit juice crystals and to provide insights into the measures which might be taken to effectively market citrus crystals of any flavor.

The resulting study has been conducted under contract with a private research firm. It was undertaken with the financial support of the Florida Citrus Commission and ARS. The Florida Citrus Commission also obtained cooperation from the Riegel Paper Corporation of New York City for the packaging of the crystals, which were put in pre-formed yellow and green pouches in laminated paper-foil-polyethylene material. Each

pouch contained enough crystals to reconstitute into a little over a pint of juice by adding 16 ounces of water. The sweetened crystals had a Brix acid ratio of 13.5, the unsweetened 9.5.

Respondents were selected from a probability sample of households in the Standard Metropolitan Statistical Area (SMSA) of Pittsburgh, Pa. The sample was designed to yield about 400 product placements--200 among homemakers who said grapefruit juice had been used in their homes at least once during the preceding 6 months and 200 who said it had not. The first interview with the homemaker was to obtain her opinions about grapefruit juice in general and her reaction to the concept of crystals. Each respondent was then given a supply of either sweetened or unsweetened grapefruit juice crystals, and asked to serve the juice to each household member 12 years of age or older. About a week later, the interviewer returned to obtain information about the homemaker's reactions to the crystals and leave sweetened

^{1/} Southern Utilization Research and Development Division, ARS.

crystals where unsweetened had already been tested and vice versa. The interviewer later obtained opinions about the second package of crystals. Both times all of the household members 12 years of age and over were asked to fill out cards on which they indicated their comments and rated the crystals and grapefruit juice in general on a nine-point hedonic scale.

The interviewing was in May and June 1967. The initial interview was completed with approximately 450 homemakers. Cooperation in testing both types of crystals was maintained with 374 households.

Approximately four households in ten reported that grapefruit juice had been used in the preceding 6 months, and about two-thirds of the users indicated grapefruit juice was served in their households at least once a week on the average.

All users were asked about the advantages and disadvantages of canned and frozen concentrated grapefruit juice. Among these homemakers, six in ten said that ease of preparation or serving is the main advantage of the canned form.

While taste or flavor was considered an advantage by only one in ten for the canned form, about four in ten mentioned taste or flavor when discussing advantages of the frozen concentrated form.

Better than half the respondents indicated they had used a powder or crystal form of drink. Those homemakers who had used any kind of powder or crystal were asked their opinions about the advantages and disadvantages of such products. They were considered easy, fast, and quick to prepare, a task the children could do. The fact that as much or little as needed could be made at one time was also considered an advantage, and ease of storage was mentioned frequently. Those who had used this type of product were just about as likely to be critical of the taste or flavor as they were to consider it an advantage. Approximately one in four spoke favorably of the taste or flavor, while one in four made negative comments about it.

Before respondents were informed that we would like to have them try a new juice product, grapefruit juice crystals were described. Respondents were then asked,

"How likely would you be to try this kind of product?" Almost 40 percent of the users said they would definitely like to try it, and the same proportion said that they would probably be interested in trying it. Approximately half of the nonuser homemakers also indicated interest in trying grapefruit juice crystals.

Many of the advantages and disadvantages homemakers ascribed to the idea of the crystals were similar to the reactions to powdered drinks on the market.

Relatively few (less than one in five) mentioned taste or flavor as presumed advantages, and about one in five assumed that the taste or flavor of a crystal product would not be as good as other forms of grapefruit juice.

The ratings given by household members after tasting the crystals tended to parallel the results from the sensory evaluation laboratory, with crystals scoring lower than regular grapefruit juice. The sweetened crystals seemed to be liked a little better than the unsweetened version by individuals who did not usually drink grapefruit juice; there was no appreciable difference in the ratings of the sweetened and unsweetened versions among grapefruit juice drinkers.

In response to a question on what they particularly liked about the crystals, approximately three household members in ten commented favorably on the taste or flavor, but better than four in ten indicated that there was nothing they especially liked. And in response to a question on dislikes, roughly half were critical of the taste or flavor. Only one-third said that there was nothing they disliked about the crystals.

When only the homemaker was considered, the pattern of ratings was essentially the same, with crystals scoring below other forms of grapefruit juice and with the sweetened form of crystals outscoring the unsweetened form. The advantages and disadvantages cited by the homemakers were also quite similar to what all household members said they especially liked or disliked. But roughly half the homemakers volunteered favorable comments about preparation or serving, saying the crystals were convenient and easy to use, or that they mixed well. Less than one homemaker in ten mentioned any difficulty in getting the crystals

to dissolve well or quickly. When asked specifically about whether the crystals were easy or hard to mix, one-third of the homemakers indicated the crystals presented some difficulties, and in a comparison of the grapefruit juice usually used with the crystals on ease of preparation, about one-half chose their regular grapefruit juice, one-third thought the crystals were easier, and the remainder (16 percent) had no preference.

The homemakers were asked how likely they would be to buy the grapefruit juice crystals if they were available in local stores and what they would be willing to pay. Answers to questions such as this cannot be taken literally as predictors of future purchases. However, they do indicate interest in a product.

Just about half of the users and one-third of the nonusers of grapefruit juice indicated they definitely or probably would purchase crystals if they were available. About one in four said they would definitely not buy them, and the remainder were divided among those who were undecided or thought they probably wouldn't purchase the crystals.

When asked the highest price she would be willing to pay for enough grapefruit juice crystals to reconstitute into a quart of juice, if grapefruit juice in general were selling for 32 cents a quart, almost half the respondents thought they would pay as much or more for the crystals as for regular grapefruit juice.

Among the grapefruit juice users who said they would consider purchasing the crystals, the majority indicated they thought more than half of their purchases of grapefruit juice would probably be of the crystals rather than the form they were currently using.

When asked about possible improvements, roughly six in ten suggested improving the taste or flavor. The only other suggestion made by as many as 15 percent was concerned with making the product easier to mix or making it dissolve more readily.

The data revealed that even among those homemakers who thought they would be interested in buying crystals, a large proportion were somewhat critical of the flavor. The product characteristics which appealed to them seemed to be the several conveniences offered by this form: Nonrefrigerated storage, space-saving, and being able to mix the desired quantity for a serving.

All-in-all, then, the results among a sample of homemakers in Pittsburgh, Pa., suggest that the concept of crystals was generally well received, but that there are still some product problems. Improving the flavor, for example, would probably enhance the chances of successfully marketing the crystals. The fact that the sweetened crystals fared somewhat better in the ratings suggests one possible direction of efforts at flavor improvement. And developing a product that would dissolve more easily would probably also help to increase its popularity, although to a lesser extent.

FLAVOR EXTRACTION WITH LIQUID CO₂

by

J. M. Randall and A. I. Morgan, Jr.
Western Utilization Research and Development Division
Albany, Calif.

(Presented by A. I. Morgan, Jr.)

Flavor components of citrus products can be extracted at room temperature by direct contact with liquid carbon dioxide. The extraction must be carried out in a pressurized system (700-800 lb./in.²), for liquid CO₂ cannot exist at lower pressures at ambient temperatures. Liquid carbon dioxide is a good solvent for many of the higher molecu-

lar weight flavor constituents of juices and has the added advantage that it is nontoxic and is easily separated from both the extract and raffinate by reducing the system pressure to one atmosphere. The CO₂ vaporizes rapidly with little residual dissolved in the liquid.

There are several other vapors with critical points around room temperature. Some of these could possibly be employed for extraction as liquified vapor under high pressure, but carbon dioxide was chosen for several characteristics. It is desirable for its selectivity, nontoxicity, and safety.

A versatile, continuous extraction system has been set up in our laboratory. The equipment was designed for a 1,000 p. s. i. working pressure and can operate with either cocurrent or countercurrent circulation. The CO₂ circulating system is equipped with stripping and condensing columns to vaporize and recondense the carbon dioxide, leaving the extracted flavor components and dissolved water behind as an extract, or "essence." Very little of the extracted flavor is vaporized with the CO₂, for the temperature variations are quite small. The extraction is carried out at 25° C., while the vaporization is at 28° C., and the condensation is at 22° C. The critical temperature of CO₂ is 31° C.

Liquid CO₂ is a nonpolar liquid which is especially useful in extracting other nonpolar compounds such as hydrocarbons. Higher molecular weight polar compounds are also easily extracted. Alcohols, ketones, esters, and aldehydes may be almost completely extracted if they contain five or more carbon atoms. The highly polar, low molecular weight compounds, such as ethyl alcohol, could probably never be extracted to any extent. Sugars and acids exhibit very little solubility in liquid CO₂ and are virtually not extracted.

To point out the increasing selectivity of CO₂ for molecules of increasing molecular weight in a homologous series, distribution coefficients, between liquid CO₂ and water, of members of the aliphatic alcohol series are shown. The distribution coefficient gives the rates of concentration, at equilibrium, of a compound in the CO₂ phase to the same compound in the aqueous phase.

<u>Alcohol</u>	<u>Distribution Coefficient</u>
n-propanol	0.34
n-butanol	3.1
n-pentanol	12
i-pentanol	10.5
n-hexanol	37
n-heptanol	125

The list of distribution coefficients indicates that the C₅ compounds can be easily extracted, while the C₄ compounds are marginal. The distribution coefficient for d-limonene, a major constituent of orange peel, is about 55, showing that it can be almost completely extracted. Liquid CO₂ extracts some color from orange juice, for the CO₂ becomes yellow during extraction. The extent of color extraction has not been determined.

The extraction of juices could be cycled until the extract was as concentrated as desired if it were not for the dissolved water carried by the CO₂ phase. This solubility, though small, limits the extraction. Water is soluble in liquid CO₂ to the extent of about 1 percent by weight, and this water remains in the extract when the CO₂ is evaporated. The concentration of the aroma is limited by this water carryover. However, aromas of the magnitude of 150,000-fold have been achieved with some products, although not yet with orange.

DISCUSSION

Question: Can you give an opinion of the quality of this essence in comparison to that obtained by conventional methods?

A. I. Morgan, Jr.: We haven't gotten far enough along to answer that question. Only informal comparisons have been made.

Question: When you spray the orange juice, do you spray below the surface of the carbon dioxide?

A. I. Morgan, Jr.: We've sprayed the juice both above and below the surface.

Question: What is the gas phase in the foam that forms? Is it an emulsion rather than a foam?

A. I. Morgan, Jr.: We have assumed that the gas phase is carbon dioxide. The mixture appears to be a foam, but we have not studied the matter extensively.

Question: What about cost? Is it greatly over other materials?

A. I. Morgan, Jr.: I've heard this discussed and I really don't believe we have an

answer. Loss of carbon dioxide is less than 10 percent, so this cost item will not be high.

As far as pressurizing is concerned, I'm afraid you've caught me without an answer.

JUICE CONCENTRATION BY REVERSE OSMOSIS

by
R. L. Merson and A. I. Morgan, Jr.
Western Utilization Research and Development Division
Albany, Calif.

(Presented by R. L. Merson)

Orange juice can be concentrated without adding heat or losing orange solids by a membrane process called reverse osmosis. Furthermore, most of the orange aroma is retained.

In reverse osmosis water diffuses under pressure through a semipermeable membrane. The success of the process for juice concentration depends upon the selectivity of the membrane and upon the rate of water removal. Selectivity is the ability of the membrane to pass water but retain dissolved solutes and suspended solids; it is determined by the chemical composition of the juice and of the membrane. For the cellulose acetate membranes now in use, fruit sugars and acids are well retained even at relatively high water permeation rates. In general, the aroma compounds of fruit juices are more difficult to retain but orange aroma is an exception. The oil soluble constituents of orange aroma do not permeate the membrane and are completely retained. Chromatographic analysis shows that a fraction of the small, water-soluble esters, aldehydes, and alcohols are lost through the membrane, particularly at high water removal rates. In spite of this, a concentrate prepared by reverse osmosis retains at least three times as much of the water-soluble aroma as does a concentrate made with cut-back juice and thus retains an excellent fresh orange flavor.

The permeation rate is not independent of selectivity, but depends on how the membrane is made. Tight membranes, which retain the water-soluble volatiles best, have low water removal rates, resulting in a longer product residence time and a more expensive process. Membranes made with higher permeation rates require less membrane surface, or lower pressures,

and hence lower equipment costs, but can result in the loss of some volatiles or even dissolved solids. Sugar solutions of low osmotic pressure can be concentrated with excellent sugar retention at rates up to 30 gallons per square foot per day. As the osmotic pressure of the feed increases, the permeation rate decreases according to the formula

$$\text{Permeation rate} = KA(P - \Delta\pi)$$

where P is the hydrostatic pressure applied to the feed, $\Delta\pi$ is (approximately) the osmotic pressure of the feed, A is the membrane surface area, and K is a permeation coefficient characteristic of the membrane. The osmotic pressure of a fourfold orange juice concentrate is about 1,300 p. s. i. Pressures necessary to produce practical permeation rates are, therefore, at least 1,500 p. s. i. or higher. Suspended solids do not seriously interfere with reverse osmosis concentration.

There is no evidence at present that membrane life is a limiting factor in juice concentration by reverse osmosis. Periodic cleaning of the membrane equipment will be necessary, of course, and since cellulose acetate membranes are inexpensive, replacement of membranes in the dismantled equipment should not be costly.

A device has been designed--WURSTACK--which combines high strength with sanitary construction. This unit contains a high proportion of membrane surface to juice holdup--thus keeping residence time of the concentrate low. This design is presented and is recommended for Research and Development use at least.

DISCUSSION

Question: Have crosslinked films been used?

R. L. Merson: We have not used them to any great extent. We looked at some polyacrylamide membranes. We find films which should have considerable selectivity, but we can't make membranes out of them.

Comment: Well, this might not be true of the crosslinked films.

Question: Do you find that oil clogs up the membrane?

R. L. Merson: No. Things do not go into the membrane and in that sense they do not plug up the membrane. In some materials--lemon juice is an example--one can get concentration of oil at the wall. The oil will coat out on the surface of the membrane, and since water is very insoluble in the oil, this does affect the diffusion rate quite markedly. This oil layer must be wiped off physically as it does not come off well with detergents.

Comment: We have defined some problems you probably know about. First, there is the essence problem. We used Florida Valencias, and our loss of essence has been considerable. Another problem is gradient density of the solute on the surface, and we hope for some sort of mechanical agitation to take care of it, but none is now known. We have used the same membrane--the Loeb type. We took the pressure up to 1,500 p. s. i. then let it down to zero and back up seven times and reduced the flux by a factor of five. Apparently,

the membrane gets compressed because of the enormous pressures, tenfold to fifteenfold above that needed for saline water. One way to get around that is to use more inexpensive membrane, and if you use inexpensive membrane, you can use lower pressures and get lower flux. Less expensive membranes may solve the present cost problem. Then, there is the problem of equipment and the plate and frame arrangement is among the most expensive method in filtration. Capital costs reduction would have to accompany lower membrane costs, say 2 years from now. Then consideration should be given to the wrapped spiral arrangement where there is a lot of membrane in a small piece of hardware. Those are some of the problems we hope you solve.

R. L. Merson: I just won't attempt to answer all this. We are aware of problems in these areas.

Question: Do you use the straight cellulose acetate membrane or do you modify it?

R. L. Merson: We use the Loeb type membrane which has a very thin skin of the regular dense cellulose acetate on the order of 2,000 angstroms, and the rest of the membrane, which gives it some strength, is very coarse, open, and nonselective. I might say we have some very promising results with maple sap that starts at a very low concentration, and they have had very little trouble with contamination.

ATTENDANCE LIST

Arrowsmith, Kent, Miles Chemical Co.,
3655 Aldes Dr., Decatur, Ga. 30032

Attaway, Dr. John, Florida Citrus Comm.,
Lake Alfred, Fla. 33850

Baker, Robert A., Fruit and Veg. Prod.
Lab., Winter Haven, Fla. 33880

Barabas, L. J., Minute Maid Co., R/D
Lab., Plymouth, Fla. 32768

Barron, R. W., Florida Citrus Comm.,
Lake Alfred, Fla. 33850

Bates, Robert P., Univ. of Fla., Food Sci-
ence Dept., Gainesville, Fla. 32603

Beck, Karl, Abbott Laboratories, 14th &
Sheridan Rd., North Chicago, Ill. 60064

Bernard, E. H., FMC Corp., P. O. Box
1708, Lakeland, Fla. 33801

Berry, Dr. Robert E., Fruit and Veg. Prod.
Lab., Winter Haven, Fla. 33880

Bertrand, Lewis, Amazon Development
Corp., Casilla 627, Quito, Ecuador

Bissett, Owen, Fruit and Veg. Prod. Lab.,
Winter Haven, Fla. 33880

Blair, James G., Florida Citrus Comm.,
Lake Alfred, Fla. 33850

- Bradner, Saidee E. , HiAcres Concentrate, Inc. , Box 7127, Orlando, Fla. 32802
- Brent, Dr. J. A. , Coca-Cola Co. , Atlanta, Ga. 30300
- Brown, J. W. , Pasco Packing Co. , Dade City, Fla. 33525
- Bruemmer, Dr. Joseph H. , Fruit and Veg. Prod. Lab. , Winter Haven, Fla. 33880
- Bucek, Wesley A. , Minute Maid Co. , Plymouth, Fla. 32768
- Buslig, Bela S. , Florida Citrus Comm. , Lake Alfred, Fla. 33850
- Carrenco, P. A. , South Puerto Rico Sugar Co. , Fellsmere, Fla. 32948
- Carroll, E. A. , Continental Can Co. , 1350 W. 76th St. , Chicago, Ill. 60620
- Carter, R. D. , Cypress Gardens Citrus Prod. , Inc. , P. O. Box 1312, Winter Haven, Fla. 33880
- Chambers, Melvin, Fruit and Veg. Prod. Lab. , Winter Haven, Fla. 33880
- Chism, Grady W. , Jr. , Corn Prod. Sales Co. , 921 East Ida St. , Tampa, Fla. 33601
- Clark, Charles Wesley, Minute Maid Co. , Plymouth, Fla. 32802
- Coleman, Richard, Fruit and Veg. Prod. Lab. , Winter Haven, Fla. 33880
- Dennison, Dr. R. A. , Univ. of Fla. , Food Tech. Dept. , Gainesville, Fla. 32603
- Dorsky, Julian, Givaudan Corp. , 125 Delawanna Ave. , Clifton, N. J. 07014
- Dubois, C. W. , Minute Maid Co. , Plymouth, Fla. 32768
- Dwin, Alfred D. , Amazon Development Corp. , Casilla 627, Quito, Ecuador
- Edwards, George J. , Citrus Expt. Sta. , Lake Alfred, Fla. 33850
- Estes, D. L. , Libby, McNeill & Libby, Ocala, Fla. 32670
- Fellers, Paul J. , Florida Citrus Comm. , Lake Alfred, Fla. 33850
- Fisher, Dr. C. H. , Sou. Util. Res. & Dev. Div. , P. O. Box 19687, New Orleans, La. 70119
- Froscher, James L. , Fruit and Veg. Prod. Lab. , Winter Haven, Fla. 33880
- Gardner, Wes, USDA, Consumer & Marketing Res. , 100 Bell Place, Winter Park, Fla. 32789
- Gerwe, Dr. Ray D. , FMC Corp. , P. O. Box 1708, Lakeland, Fla. 33801
- Gray, L. E. , FMC Corp. , P. O. Box 1708, Lakeland, Fla. 33801
- Griffiths, Dr. J. T. , Cypress Gardens Citrus Prod. , Inc. , Box 1312, Winter Haven, Fla. 33880
- Griggs, T. W. , Orange Crystals Div. , Plant Indus. , Plant City, Fla. 33566
- Hartman, Gordon D. , Tropicana Prod. , Inc. , Box 338, Bradenton, Fla. 33505
- Hastings, Kenneth W. , Lake Hamilton Concentrate, Inc. , Bartow, Fla. 33830
- Hill, E. C. , Florida Citrus Comm. , Lake Alfred, Fla. 33850
- Hoffer, Douglas R. , Florida Citrus Comm. , 1115 Memorial Blvd. , Lakeland, Fla. 33802
- Hoover, Dr. Sam R. , Nutr. , Consum. , and Indus. Use Res. , ARS, USDA, Washington, D. C. 20250
- Horn, L. J. , National Dairy Prod. Corp. , 801 Waukegan Rd. , Glenview, Ill. 60025
- Hostettler, James B. , Minute Maid Co. , Plymouth, Fla. 32802
- Huber, Miss Dorothy Ann, Continental Can Co. , Metals R & D, 1350 W. 76th St. , Chicago, Ill. 60620
- Huffman, C. F. , Minute Maid Co. , Plymouth, Fla. 32802
- Hughes, Sidney E. , Fruit and Veg. Prod. Lab. , Winter Haven, Fla. 33880

Hunter, Dr. G. L. K., Minute Maid Co.,
Orlando, Fla. 32802

Ismail, Mohamed A., Florida Citrus
Comm., Lake Alfred, Fla. 33850

Jahn, Otto L., USDA, Market Quality Res.
Div., Orlando, Fla. 32803

Jefferson, Jon E., Redd Laboratories, 1711
S. 10th St., Safety Harbor, Fla. 33572

Jenne, Robert, Abbott Laboratories, 14th &
Sheridan Rd., North Chicago, Ill. 60064

Kesterson, James W., Citrus Exp. Sta.,
Lake Alfred, Fla. 33850

Kew, Theo. J., Fruit and Veg. Prod. Lab.,
Winter Haven, Fla. 33880

Kilburn, R. W., Florida Citrus Cannery
Coop., Drawer 1111, Lake Wales, Fla.
33853

Lambert, Albert J., Abbott Laboratories,
14th & Sheridan Rd., North Chicago, Ill.
60064

Lastinger, J. C., Jr., Fruit and Veg. Prod.
Lab., Winter Haven, Fla. 33880

Lewis, J. Arthur, 7524 S.W. 53rd Ave.,
South Miami, Fla. 33143

Lime, Bruce, Food Crops Util. Res. Lab.,
P. O. Box 388, Weslaco, Tex. 78596

Linstrom, Hal, Econ. Res. Div., Sou. Util.
Res. & Dev. Div., P. O. Box 19687, New
Orleans, La. 70119

Logan, C. W., Minute Maid Co., Plymouth,
Fla. 32802

Lund, Eric D., U. S. Fruit and Veg. Prod.
Lab., Winter Haven, Fla. 33880

McAllister, J. W., USDA, Consumer &
Market. Serv., P. O. Box 860, Winter
Haven, Fla. 33880

McDuff, O. R., Adams Packing Assoc.,
P. O. Box 37, Auburndale, Fla. 33823

McKinney, Samuel, Tropicana Prod., Inc.,
1527 Carorella Circle, Sarasota, Fla.
33578

McKinnis, Dr. R. B., Brown Citrus Machin-
ery Corp., Winter Haven, Fla. 33880

MacDowell, L. G., Florida Citrus Comm.,
P. O. Box 148, Lakeland, Fla. 33801

Marotti, Gene, Cypress Gardens Citrus
Prod., Inc., Winter Haven, Fla. 33880

Matthews, R. F., Univ. of Fla., Food Sci.
Dept., Gainesville, Fla. 32603

Merson, R. Larry, Western Util. Res. &
Dev. Div., 800 Buchanan St., Albany,
Calif. 94710

Meunier, Vincent, Rohm & Haas, Charlotte,
N. C. 28201

Miller, Don P., Treesweet Prod. Co., P. O.
Box 189, Fort Pierce, Fla. 33451

Miller, W. H., Fruit and Veg. Prod. Lab.,
Winter Haven, Fla. 33880

Moore, Dr. E. L., Florida Citrus Comm.,
Lake Alfred, Fla. 33850

Moshonas, M. G., Fruit and Veg. Prod.
Lab., Winter Haven, Fla. 33880

Moshy, Raymond J., American Machine and
Foundry Co., Springdale, Conn. 06879

Muncie, Dr. F. W., Suni-Citrus Products,
Haines City, Fla. 33844

Murdock, D. I., Minute Maid Co., Plymouth,
Fla. 32768

Murtaugh, Thomas M., Pet, Inc., Greenville,
Ill. 62246

Nagel, George M., Redd Laboratories, 1711
S. 10th St., Safety Harbor, Fla. 33572

Naguib, Shahier, Winter Garden Citrus Prod.
Coop., Winter Garden, Fla. 32787

Neubert, Dr. A. M., Fruit and Veg. Prod.
Lab., Winter Haven, Fla. 33880

Newhall, Dr. William F., Citrus Expt. Sta.,
Lake Alfred, Fla. 33850

Nordby, Harold E., Fruit and Veg. Prod.
Lab., Winter Haven, Fla. 33880

- Parish, Elmer C. , Crown Cork & Seal Co. ,
2806 Lion Heart Rd. , Winter Park, Fla.
32789
- Perkins, J. F. , Firminich, Inc. , 277 Park
Ave. , New York, N. Y. 10001
- Pinner, Ann S. , USDA, Consumer & Market-
ing Serv. , P. O. Box 860, Winter Haven,
Fla. 33880
- Postlmayr, H. L. , Minute Maid Co. ,
Plymouth, Fla. 32802
- Potter, R. , Givaudan Flavors, 321 West
44th St. , New York, N. Y. 10001
- Potty, V. H. , Fruit and Veg. Prod. Lab. ,
Winter Haven, Fla. 33880
- Praschan, V. C. , National Dairy Prod.
Corp. , 801 Waukegan Rd. , Glenview, Ill.
60025
- Prieto, Juan, M. C. Varona & Assoc. , 1195
Bay Dr. , Miami Beach, Fla. 33141
- Ratcliff, Morris W. , Florida Citrus Cannery
Coop. , Lake Wales, Fla. 33853
- Reitz, Dr. Herman J. , Citrus Expt. Sta. ,
Lake Alfred, Fla. 33850
- Richardson, Dale, Florida Citrus Cannery
Coop. , Lake Wales, Fla. 33853
- Robbins, R. C. , Univ. of Fla. , Gainesville,
Fla. 32603
- Roberson, John P. , Chas. Pfizer & Co. ,
Inc. , 1370 Valley View Rd. , Dunwoody,
Ga. 30043
- Roe, Bongwoo, Fruit and Veg. Prod. Lab. ,
Winter Haven, Fla. 33880
- Rogers, J. A. , Fritzsche Bros. , Inc. ,
New York, N. Y. 10001
- Rouse, A. H. , Citrus Expt. Sta. , Lake
Alfred, Fla. 33850
- Schulz, H. E. (Bert), Florida Chemical Co.,
Inc. , Lake Alfred, Fla. 33850
- Shaw, Dr. Philip E. , Fruit and Veg. Prod.
Lab. , Winter Haven, Fla. 33880
- Smith, C. B. , Plymouth Citrus Prod. Coop. ,
Plymouth, Fla. 32768
- Stephens, Charles E. , The Coca-Cola Co. ,
310 North Ave. , Atlanta, Ga. 30301
- Sutherland, C. Reed, Birds Eye Div. , Gen.
Foods, Inc. , Winter Haven, Fla. 33880
- Sutton, Earl W. , FMC Corp. , P. O. Box
1708, Lakeland, Fla. 33801
- Swift, Dr. Lyle J. , Fruit and Veg. Prod.
Lab. , Winter Haven, Fla. 33880
- Talarico, George, Givaudan Corp. , 125
Delawanna Ave. , Clifton, N. J. 07014
- Tatum, James H. , Fruit and Veg. Prod.
Lab. , Winter Haven, Fla. 33880
- Thompson, Edward R. , USDA, Consumer
& Market. Res. , Washington, D. C.
20250
- Ting, Dr. S. V. , Florida Citrus Comm. ,
Lake Alfred, Fla. 33850
- Trumm, Howard W. , Golden Gem Growers,
Inc. , Umatilla, Fla. 32784
- Tucker, David, Univ. of Fla. , Ext. Serv. ,
Lake Alfred, Fla. 33850
- Vandercook, Carl E. , Fruit and Veg. Chem.
Lab. , Pasadena, Calif. 91101
- Veldhuis, Dr. M. K. , Fruit and Veg. Prod.
Lab. , Winter Haven, Fla. 33880
- Viale, Hector, Adams Packing Assoc. ,
Auburndale, Fla. 33823
- Wagner, C. J. , Jr. , Fruit and Veg. Prod.
Lab. , Winter Haven, Fla. 33880
- Walker, Marvin H. , Florida Citrus Cannery
Coop. , Lake Wales, Fla. 33853
- Watkins, Wayne J. , Tropicana Prod. Inc. ,
Bradenton, Fla. 33505
- Weidenhamer, Margaret, Standards and Res.
Div. , Statis. Reporting Serv. , USDA,
Washington, D. C. 20250
- Wenzel, Dr. F. W. , Citrus Expt. Sta. ,
Lake Alfred, Fla. 33850

Westbrook, Dr. George F. , Florida Dept. of
Agr. , Winter Haven, Fla. 33880

Winrow, Myrna, Fruit and Veg. Prod. Lab. ,
Winter Haven, Fla. 33880

Williams, L. D. , Corn Prod. Co. , Moffett
Tech. Center, Argo, Ill. 60501

Wojcik, B. H. , South, Util. Res. and Dev.
Div. , P. O. Box 19687, New Orleans,
La. 70119

Williard, Robert P. , Adams Packing Assoc. ,
Auburndale, Fla. 33823

Wilson, C. W. , III, Fruit and Veg. Prod.
Lab. , Winter Haven, Fla. 33880

Wolford, Richard W. , Florida Citrus Comm. ,
Lake Alfred, Fla. 33850

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FOOD CROPS UTILIZATION RESEARCH LABORATORY

P. O. Box 388
Weslaco, Tex. 78596

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WESTERN REGIONAL RESEARCH LABORATORY

800 Buchanan Street
Albany, Calif. 94710

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FRUIT AND VEGETABLE CHEMISTRY LABORATORY

263 South Chester Avenue
Pasadena, Calif. 91106

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