

reagents. It was found that the absorption of oxygen took place slowly and was in no case complete in a reasonable length of time. In a typical experiment, the absorption at the end of 3 minutes amounted to 8.4 per cent, at the end of 6 minutes 14.8 per cent, and at the end of 9 minutes 20.4 per cent. Increasing the time of contact of the gas and reagent did not result in any appreciable change in the volume of the sample. That the absorption of oxygen was actually incomplete was shown by treatment of the residue with alkaline pyrogallol, whereupon a further decrease of 0.4 per cent was obtained, thus indicating approximately the correct percentage of oxygen in air. It appears, therefore, that the solution of phosphorus in castor oil is not suitable for the gas-analytical determination of oxygen at ordinary temperatures. No attempt was made to maintain the reagent at an elevated temperature in order to obtain complete absorption, since it is believed that such a procedure would complicate the determination of oxygen unnecessarily. Assuming that complete absorption can be obtained with this reagent at elevated temperatures, there seems to be no reason why it should be preferred to alkaline pyrogallol properly prepared.¹ In fact the latter reagent is much more convenient to prepare, and by its use practically complete absorption of oxygen can be obtained at room temperatures in a much shorter time.

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THE UTILIZATION OF CULL FLORIDA CITRUS FRUITS²

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In the packing of citrus fruits, a considerable proportion of the fruit coming into the packing houses is unfit for shipment, and must be discarded; this discarded fruit constitutes the culls, and may amount, during poor seasons, to as much as 10 per cent of a given lot of fruit, though ordinarily the proportion is not so high. The usual causes of culling are extreme over- or under-size, stem-end rot, traumatic injuries to the peel, and blue molds. A few of these culls are disposed of at low prices for quick sales in the local markets, while a good proportion are consumed by the local cattle or simply allowed to decay on the ground. A considerable number of these culls have the flavor and food value unimpaired, if utilized immediately. The main problems offered were (a) to find a satisfactory process by which the juice of these culls could be preserved for at least two years, without conflict with the national or state pure food laws, and (b) to develop a method by which the flavoring oil could be removed from the peels in such a manner that the product would meet the commercial requirements for such an oil, and could sell,

¹ THIS JOURNAL, 7 (1915), 587 and 8 (1916), 131.

² Author's abstract of a rather extensive report on the utilization of the cull citrus fruits from the packing houses in Florida, covering the author's work on this subject during the period from October, 1911, to August, 1913, under the auspices of the Florida Citrus Exchange, at the Mellon Institute of Industrial Research, of the University of Pittsburgh. Publication has been withheld, up to this time, in accordance with the fellowship agreement; complete publication of the entire report will be made at a later date.

as a domestic product, in competition with the imported Italian oil. The recovery of the citric acid formed one of the minor problems.

A large number of experiments were made with different processes to determine their effect on the stability of the juice. As had already been observed, it was soon found that simple pasteurization of the juice was not sufficient to protect it from further change; for a short time after pasteurization, usually less than two weeks, the juice kept without apparent change, but after the lapse of this time a change of color became evident, the juice darkening and finally becoming muddy; this change in color was accompanied by a deterioration in flavor, which eventually became offensively acid. All specimens did not change to the same degree, but it was found impossible to correlate this difference between specimens with differences in acidity or sugar content. Such darkened specimens appeared to be sterile, no organisms being shown by inoculations on standard agar or on sterilized orange juice, or under microscopic examination. The effect seemed to be due to chemical action, but although a large number of tests were made, these failed to indicate just what change had taken place in the darkened juice. It was found, however, that the removal of the air dissolved in the juice and that in the container above it, followed by pasteurization, was sufficient to prevent this deterioration of the juice for a considerable time—in fact all failures which occurred within two years could be traced to air having gained access to the juice through leaks which developed in the stoppers on long standing under varying conditions of temperature. It was found further that, as would naturally be expected, it was the oxygen of the air which was active in producing this change, although replacing the air with pure oxygen did not produce as rapid and strong a darkening as would be expected, the effect being but little different from that of air alone.

It may be of interest to note here that the most common organized contamination of orange juice, which was encountered in this work, was a strain of the wild yeast ("Kahmhefe") *Willia anomala*, and it is this organism which is responsible for the development of the ester odor (apparently ethyl acetate) which may so frequently be noticed in orange juice which has stood some hours at room temperature; the yeast was kindly identified for me by Dr. Alb. Klöcker, of the Carlsberg Laboratory, Copenhagen. Acetic acid bacteria were also found occasionally, in every case observed being secondary to the wild yeast, and on long standing various molds developed. The common blue molds of the peel of the orange, *Penicillium italicum* and *P. olivaceum*, appeared to be unable to grow on the sterilized juice, and all attempts to inoculate them directly from infected fruit on this medium resulted instead in the growth of the *Willia*.

The simplest method of effecting the removal of the air from and above the juice in the containers seemed to be to replace it by some non-oxidizing gas, and of those commercially possible, carbon dioxide appeared to be the best. A very large number of

specimens of orange and grapefruit juices were prepared, in which the juice was charged with carbon dioxide at atmospheric pressure, and the air above the liquid replaced with the dioxide; the bottles were then sealed with paraffined stoppers, pasteurized, and the joint between the stoppers and the necks kept covered with paraffin while cooling. This system of sealing, while by no means perfect, gave a considerable number of specimens which remained without apparent change for two years or more. Charging with CO₂ under pressure, without removal of the air present, did not afford protection against deterioration. It was found that pure nitrogen, hydrogen or methane (washed natural gas) gave as good results so far as preservation was concerned, as did the carbon dioxide, but owing to their lower solubility, they were somewhat more difficult to deal with than the dioxide. Nitrous oxide, as might be expected, gave results about like those of pure oxygen. So far as flavor is concerned, the hydrogen was superior to any of the other gases, though of course harder to handle. The carbon dioxide gave a slightly unnatural tang to the juice, suggesting incipient fermentation to some who tasted it.

Sealing *in vacuo* was also tried, and eventually proved to be the most satisfactory method of meeting the difficulty. Early experiments using sealing bottles showed that the juice retained its flavor best when pasteurized under as complete a vacuum as possible, the usual process being to exhaust the container to about 28.5 inches vacuum, while immersed in water at a temperature slightly above the boiling point at this pressure; the contents were then allowed to boil a little while under the reduced pressure, to drive out dissolved gases, the liquid then cooled, and the bottle sealed. Such preparations kept excellently, as long as the bottles remained sealed; breakage of the seal was followed by discoloration and deterioration of flavor, as in the fresh juice. Later experiments were made using the method of vacuum sealing with a rubber gasket and cap, which has been so widely applied recently in the preparation of food products, especially by the Beech Nut Company. It was found that equally good results were obtained, the main difference in operation being that the juice in the container was heated to a point slightly above that at which it would boil at the vacuum employed, then the container placed in the sealing machine, exhausted, ebullition permitted for a minute or so, and then the jar sealed and pasteurized. Of course, these seals fail occasionally, and such failures were always evidenced by discoloration of the juice.

What has been said heretofore has referred mainly to orange juice; the juice of the grapefruit undergoes exactly the same discoloration and change of flavor, on simple pasteurization in air, as does the orange juice. Lemon juice, however, seems to be a somewhat different proposition, as it is reported in the literature that repeated simple pasteurization is all that is necessary to prevent deterioration; no direct experiments were made with lemon juice, but it was found that the repeated pasteurization (pasteur-

ized at 63-65° C. on two or even three successive days) was insufficient to inhibit this change in orange juice.

The temperature of pasteurization is an important factor in the flavor of the juice. Temperatures below 60° C. were insufficient to prevent the development of the spores of *Willia*, and with subsequent fermentation, while at temperatures above 70° C., the flavor began to be noticeably that of cooked juice, and lacked the freshness of the untreated product. Pasteurization at 63-65° C., for 15 minutes, provided the entire volume of the juice reached that temperature, gave the most satisfactory results, so far as flavor was concerned. Sterilizing at 100° C., and autoclaving at pressure are out of the question when preservation of the natural flavor is to be considered; autoclaving without the replacement of the air by a non-oxidizing atmosphere usually caused immediate darkening, in addition to the deterioration of flavor.

For the best flavor it was found that all of the fruit should not be peeled before expressing the juice; the juice from all peeled fruit was flat and uninviting, but if five to ten per cent of the oranges were left unpeeled, the juice had about the correct flavor. Of course, the addition of the expressed oil from the peel is possible, but experiments indicated that this did not give as satisfactory a flavor as the retention of unpeeled fruit in the lot to be pressed. For grapefruit juice, it was found necessary to peel completely all the fruit, and to supply the flavoring by adding five to ten per cent of unpeeled oranges; retention of the grapefruit peels produced a liquid of extreme bitterness.

The clarification of the juice is a serious problem. For commercial purposes it would seem best that the juice be nearly clear, although this is not a natural condition for orange juice. The juice, however, does not yield readily to the ordinary methods of clarification or filtration; of many methods tried, the best results were obtained with DeLaval clarifiers, the juice being taken first through a clarifying bowl to remove the greater part of the suspension, and then through a filtering centrifuge. The liquid so obtained is not water-clear, but contains comparatively little suspension. An alternate procedure is to pasteurize out of contact with the air in large containers, and allow to settle, then draw off the clear supernatant liquid after several weeks, bottle like fresh juice, and treat the residue by centrifugal methods. Chemical clarification by means of formaldehyde or alcohol is possible, but obviously not desirable.

Both orange and grapefruit juices may be evaporated under conditions of greatly reduced pressure, to a thick sirup, and this sirup may, in either case, be dried to a brittle, glassy, and very hygroscopic solid. It is essential for the retention of a good flavor, however, that the temperature in these evaporation and drying processes shall at no time exceed 60° C., which condition makes the drying extremely slow. The products so obtained may be dissolved in water, and beverages thus made up from them; it cannot be said that

the flavor of these beverages is quite up to the standard of fresh juice preserved as above indicated, but it is still quite close to the normal taste of orange juice, if the evaporation has been carefully done. Of course, the vacuum treatment removes the flavoring materials from the juice, and it is necessary to add oil for flavoring purposes, better at the time of making the beverage than before pasteurization in the vessel. The concentrated juice will keep under the same conditions as the fresh, *i. e.*, after pasteurization in the absence of free oxygen; the dried material cannot be pasteurized, as it fuses together at pasteurizing temperatures, but pasteurization is not necessary, provided water and air are excluded.

There is a considerable literature, especially of patents, regarding the preservation of fruit juices, but it is thought inexpedient to include any of these references in this abstract.

The recovery of the flavoring oils from the peels of citrus fruits is at present carried on mainly by rather crude methods in Italy and Sicily, under conditions of cheap labor with which American packers cannot compete. A process for recovering this valuable oil from the peels of Florida oranges must therefore be one which will handle a large number of peels at very little cost. Various mechanical methods of pressing, rolling, abrading, etc., were tried without much promise of success. Soaking methods, in which the ground peel is covered with water, to the surface of which the oil rises and is there drawn off, gave low yields of fair quality oil, but while simple, these processes are rather inefficient. After considerable experimentation it was found that a very satisfactory oil could be produced by grinding the peel, submitting the ground material to a current of water vapor at greatly reduced pressure and condensing and separating the oil. Ordinary Florida oranges yielded about 0.5 cc. of oil per peel, while the late Valencias gave from 1 to 1.5 cc. per peel. The liberation of the oil appears to be favored by previous partial drying of the peel. The oil obtained from Florida oranges as above indicated, has been used repeatedly in cakes and candies, when dissolved in alcohol, and has given excellent results. It appears to be up to the requirements of the existing legislation.

As is well known, the flavoring oils from citrus fruits rapidly deteriorate on exposure to the air, especially in the light, acquiring a very offensive turpentine-like odor. It was found during this research that this could be obviated by the addition to the oil of about 10 per cent by volume of absolute alcohol; oil so treated was allowed to stand exposed to diffused daylight at room temperatures for many months, without deterioration. It is not to be recommended, however, that such oils be kept under these conditions; keeping in the dark in a cool place is far better, even with protecting agents present. The use of 1.5 to 2 per cent of olive oil has also been recommended for this purpose; this gives some protection, but is not as good as the alcohol. Sealing in an atmosphere of carbon dioxide is also effective in protect-

ing the oil for a long time. On the whole, however, the addition of absolute alcohol gave the best results, and it seems that it would be well to admit of this treatment of such oils for their preservation in the United States Pharmacopoeia and other standards.

The recovery of the citric acid from the juice of Florida citrus fruits (for the sake of the acid alone) is scarcely worth while, in view of the small amount available, rarely over 0.7 per cent in the orange, or 1.5 per cent in the grapefruit. As a matter of scientific interest, however, it was found that Wehmer's *Citromyces* molds would grow on the sterilized juice in the presence of calcium carbonate, and convert a considerable proportion of the residual sugar into citric acid. The commercial application of such a process seems rather hypothetical.

From the results of this investigation it appears, then, that the preservation of the juice of the orange and grapefruit is practicable, the method depending on pasteurization out of contact with air, and that the recovery of the flavoring oil from the peels may be accomplished commercially by methods of vacuum distillation, but that the recovery of the citric acid for itself alone is not practicable.

Since this abstract was prepared, a valuable and interesting paper by Will¹ has appeared, relating to the utilization of these culls in the California citrus industry.

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ON THE CHEMICAL CONSTITUTION OF THE PROTEINS OF WHEAT FLOUR AND ITS RELATION TO BAKING STRENGTH

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INTRODUCTION

The most generally accepted definition of "baking strength" of a wheat flour is that put forward by Humphries and Biffen,² in 1907, which states that a "strong wheat is one which yields flour capable of making large, well-piled loaves;" a definition similar to that of Jago,³ who states that "strength. . . . is defined as the measure of the capacity of the flour for producing a bold, large-volumed, well-risen loaf." Since the value of wheat (other things being equal) depends on the so-called "strength" of the flour which may be made from it, it is obviously of great importance that complete knowledge be obtained concerning the factors which cause strength, and to this end an enormous amount of scientific work has been done, especially during the last twenty years. In spite of the fact that some of the foremost investigators of the world have bent their energies to this task, the problem is not yet completely solved, although considerable light has been thrown on the subject. It is not yet possible to correlate baking strength with any chemical or physical factor to such an extent that a simple laboratory test or group of tests will always

¹ THIS JOURNAL, 8 (1916), 78-86.

² "The Improvement of English Wheat," *Jour. Agr. Sci.*, 2 (1907), 1-16.

³ "Technology of Bread Making," Chap. XV, p. 291, 1911.