

wines which were attractive shades of red. It is still unclear if this color instability is inherent or preventable by careful manufacturing techniques.

With only one season's fermentation experience, little can be said about the seasonal consistency of specific cultivars. Working with the 1973 grape crop, we have eliminated the less promising treatments, doubled the number of cultivars examined and standardized juice extraction, must handling and aging treatments with the aim of maintaining or improving upon the quality of the wines from better cultivars and significantly upgrading the less promising ones.

The results with the 1972 crop are encouraging. A number of experimental wines were well received in formal and informal tastings. If these tasters were indeed typical of those consumers presently increasing their interest in and consumption of table wines. Southeast grape cultivars, specifically muscadine types should have a promising regional potential.

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FURFURAL AS AN INDICATOR OF FLAVOR DETERIORATION IN CANNED CITRUS JUICES*

M.D. MARAULJA and J. S. BLAIR¹

Florida Department of Citrus
and

R. W. OLSEN and F. W. WENZEL

IFAS Agricultural Research and Education
Center
Lake Alfred, Fl. 33850

Abstract. A quantitative method was needed to provide data that would indicate flavor deterioration that occurs in commercially canned citrus juices during storage. Since it had been

previously established that furfural increased in canned orange juice during storage, a colorimetric method, based on its reaction with benzidine, was used to determine furfural quantitatively in distillates from these products. To cover the wide range of flavor quality resulting from commercial storage of canned orange and canned grapefruit juices, subjective flavor scores and furfural determinations were obtained monthly for seven months during storage of these products at 40, 50, 60, 70, and 80°F. Furfural in distillates increased as flavor deterioration progressed. Correlation coefficients (r) between flavor scores and furfural from 'Hamlin' orange, 'Valencia' orange, and grapefruit juices were highly significant. Rate of flavor deterioration was dependent on both storage temperature and storage time. However, temperature was more significant than storage time. Retention time of initial flavor quality was much longer when the canned prod-

¹Previously employed by the Research Division of the American Can Company, Barrington, Ill.; partially employed, following his retirement, during 1963 and 1964 by the Florida Citrus Commission.

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ucts were stored at 60°F or lower. Subsequent analytical research during recent years at another laboratory on the rapid recovery of furfural from canned and glass-packed citrus juices and its determination, using the colorimetric reaction of furfural and aniline, are discussed briefly and recommended for use in commercial quality control laboratories.

In 1964 Blair (2) found that the aqueous phase of distillates from stored canned orange juice contained furfural when qualitatively analyzed using either ferroate or benzidine tests. The large difference in intensity of color developed in distillate from canned 'Hamlin' orange juice stored for 39 months at 80°F than that in distillate from canner 'Valencia' juice after storage for 10 months at the same temperature indicated that furfural increased in canned orange juice during storage. Previously, Natarajan and Mackinney (10) had detected furfural in orange juice stored in the presence of oxygen. Also, Kirchner and Miller (7) reported that fresh and freshly canned orange juice contained only a trace of furfural but after storage of the canned juice for 3 years at room temperature, it had increased to 5.1 mg/kg. Furfural was not detected in essences recovered from fresh Florida orange juice by Attaway *et al.* (1) or Wolford *et al.* (13).

It was also reported in 1964 by Blair (2) that a quantitative study was in progress of the rate at which furfural develops in commercially canned citrus juices during storage at various temperatures. The purpose of this paper is to describe the quantitative colorimetric method used during this investigation for determining furfural in distillates from canned orange and grapefruit juices stored at temperatures from 40 to 80°F. Also, to present the relationships found between furfural content of stored canned citrus juices and subjective flavor scores, storage temperatures and storage times. Such information had not been available prior to the completion of this study in 1965.

Materials and Methods

Canned citrus juices, storage and examination. 'Hamlin' orange, 'Valencia' orange and grapefruit juices were processed and canned in a commercial plant during the 1963-64 citrus season. Sufficient quantities of No. 2 cans of these products were obtained immediately after packing

for storage at 40, 50, 60, 70 and 80°F at the Citrus Experiment Station. Samples of these canned juices, stored at each temperature, were used monthly for furfural analyses and flavor evaluation.

Preparation of Reagents

Benzidine dihydrochloride solution. Benzidine dihydrochloride (3.35 g) was dissolved in a mixture of 325 ml of reagent grade anhydrous methanol and 60 ml of distilled water. This reagent was prepared as needed and used immediately since it can deteriorate upon exposure to light and room temperature.

Sodium acetate solutions. Citric acid monohydrate (2.0 g) and 1.0 g. of sodium acetate was dissolved in a solution containing 250 ml of glacial acetic acid, 120 ml of 4.0 N sodium hydroxide and 20 ml of distilled water. The resulting pH was 3.5. This solution was stored at room temperature and used as needed for addition to sample distillates.

Another sodium acetate solution, approximately 0.2 M, was prepared and used in making furfural standards for obtaining a calibration curve. Dry sodium acetate (27.2 g) was dissolved in 85 ml distilled water, adjusted to pH 4.6 with 15 ml glacial acetic acid and then made to 1 liter volume with distilled water.

Furfural standards. A furfural stock solution was prepared by dissolving 1.0 g of freshly distilled furfural in 1 liter of 0.2 M sodium acetate solution which had been adjusted to pH 4.6. This solution was stored in the dark at 32°F. Solutions of 100 µg/liter were prepared from the stock solution as needed. Furfural standards were prepared ranging from 50 to 300 µg/25 ml by taking aliquots of 0.5, 1.0, 1.5, 2.0, 2.5, and 3.0 ml of 100 µg/liter solution and diluting them with distilled water to 25 ml in 50 ml Nessler tubes. A calibration curve was obtained using these standards.

Sample preparation. Distillation of 1 liter of the canned juice was necessary to obtain sample of distillate for analysis. If refrigerated, the juice was allowed to come to room temperature. The pH was adjusted to 5.8 ± 0.1 with 4N sodium hydroxide solution and then transferred to a 2 liter boiling flask. Dow Corning anti-foam solution was added and the sample brought to boiling as rapidly as possible. The vapor was passed through a water-cooled spiral condenser and the cool distillate then passed through a standard Clevenger oil-trap to remove peel oil. The 50 ml of distillate was collected and divided into 2-25 ml portions, one of

which was analyzed and the other kept as a duplicate.

Determination of furfural. The 25 ml samples of distillates, furfural standards or distilled water reagent blank, were placed in 50 ml test tubes. Using an automatic pipette, $9 \text{ ml} \pm 0.2$ of sodium acetate solution, pH 3.5, was added and mixed thoroughly. Freshly prepared benzidine dihydrochloride reagent ($19 \text{ ml} \pm 0.1$) was added to each sample. The tubes were capped and inverted several times and then placed in the dark at room temperature for color development. The magenta or purplish-red color is light-sensitive and subject to some fading during development even in moderate light. Final pH was between 3.9 and 4.1 which is the optimum range for color development. After 25 minutes, light transmittance was measured through an 8.0 cm light path with a Photovolt, Model 450, Nessler Tube Colorimeter using a $530 \text{ m}\mu$ filter. All samples were transferred to the same Nessler tube, having a 20 mm inside diameter, which was always used in the colorimeter. This tube was also graduated at 1 cm intervals and had a small lip for ease of pouring. Fur-

fural values were obtained from the instrument readings by referring to the calibration curve. Duplicate analyses may be made using both 25 ml portions of distillate, the sum of which is the micrograms of furfural in 50 ml of distillate.

To convert from $\mu\text{g}/50 \text{ ml}$ distillate to $\mu\text{g}/\text{liter}$ juice, the furfural content in the distillate was multiplied by the factor 4.16. This factor was derived by the analysis of 4 samples of canned 'Valencia' orange juice varying in furfural content from 62 to 552 $\mu\text{g}/50 \text{ ml}$ distillate. Following the first 50 ml, 6-100 ml fractions of distillate from each of the 3 canned juices were also collected for analysis and the furfural content of all fractions of distillate for each sample were totaled. The amount found in the first 50 ml of distillate from each of the juices, containing different amounts of furfural, was plotted against the total micrograms per liter of juice (Fig. 1). The result was a straight line with a slope of 4.16, indicating that the total furfural content in 1 liter of stored canned juice is 4.16 times that found in the first 50 ml of distillate.

Flavor evaluation. The flavor of each of the

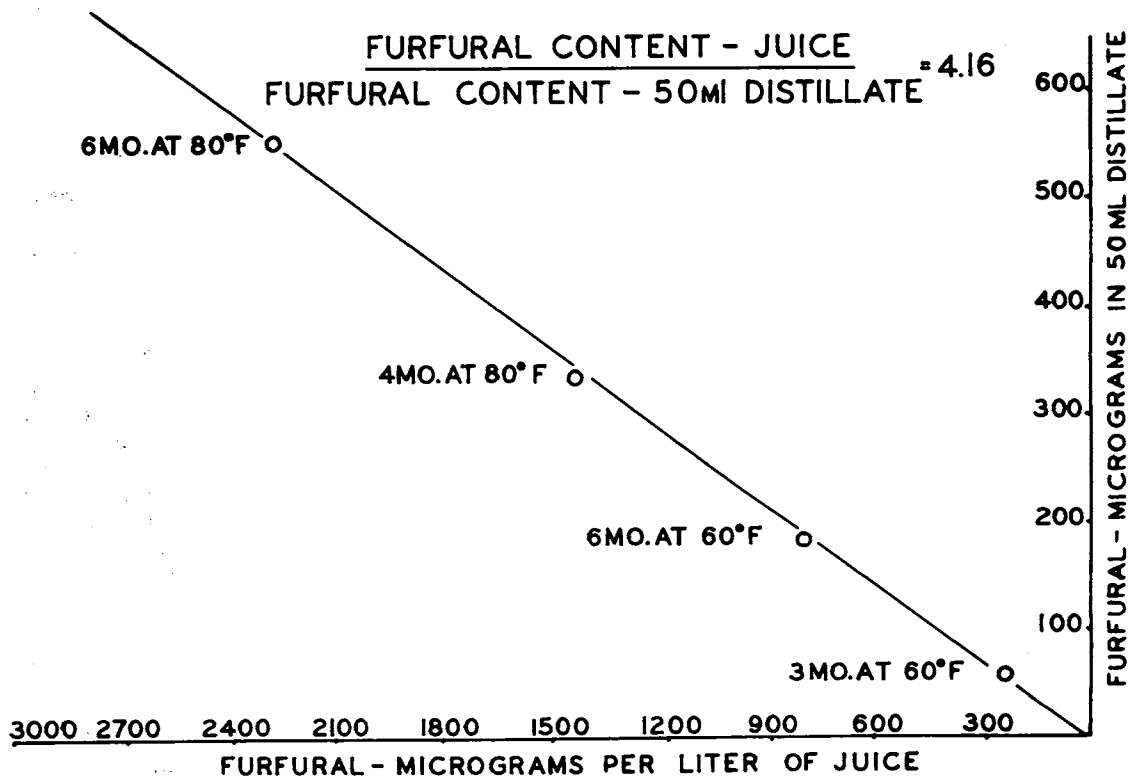


Fig. 1. Graph for conversion of micrograms of furfural in 50 ml of distillate to micrograms in 1 liter of juice.

canned juices was scored by a 10-member panel of experienced tasters. All juices, were tasted at monthly intervals at room temperature when furfural determinations were made. A 10-point scale was used ranging from 10 (excellent) to 1 (very poor). Scores of 4 or lower indicated that the tasters considered the juices not acceptable.

Results and Discussion

Results showed that furfural increased in canned 'Hamlin' orange, 'Valencia' orange and grapefruit juices during storage (Fig. 2, 3, 4). However, more important was that as the flavor deterioration increased during storage, furfural in all of the canned juices also increased (Table 1) to such an extent that correlation coefficients (r) between furfural and flavor scores were highly significant (Table 2).

Rate of furfural development in canned citrus juices was dependent on both temperature and time of storage. Correlation coefficients (Table 2) show that temperature is more significant than time of storage. Loss of flavor and increase of off-

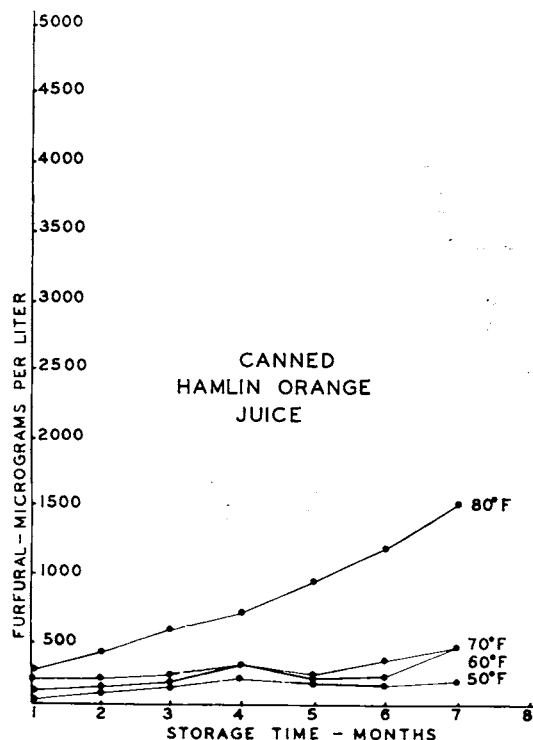


Fig. 2. Furfural content of canned 'Hamlin' orange juice after storage at various temperatures.

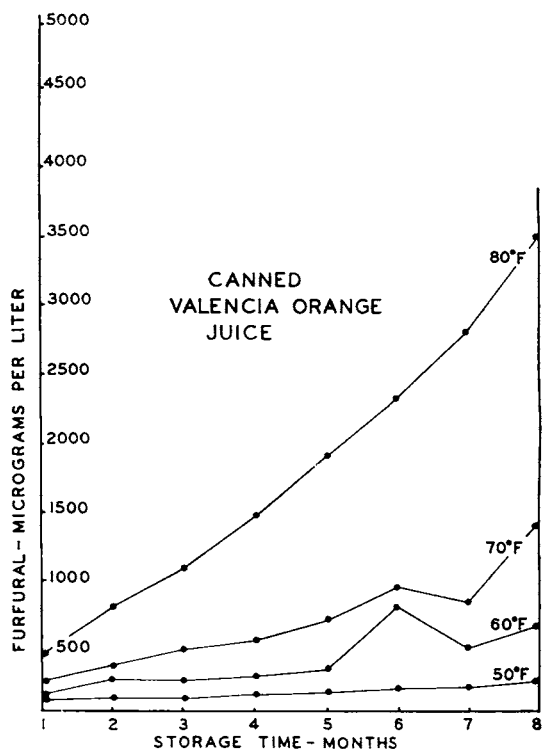


Fig. 3. Furfural content of canned 'Valencia' orange juice after storage at various temperatures.

flavors were greatest in the canned products stored at 80°F. Considering data from this study, 60°F would help greatly to prolong the storage life of commercially canned orange and canned grapefruit juices.

Rate of development of furfural in canned citrus juices was also dependent upon the variety of fruit used for packing such products. Furfural content of the different canned juices, stored under the same conditions, varied considerably, from the highest in canned grapefruit juice to the lowest in canned 'Hamlin' orange juice. Nevertheless, the rate of flavor deterioration was greater in canned 'Hamlin' orange juice than in canned 'Valencia' orange juice, both of which have less flavor stability than canned grapefruit juice. This is apparently true because of the better flavor in 'Valencia' orange juice immediately after canning than that in canned 'Hamlin' orange juice. Grapefruit juice, after canning, retains its typical flavor for longer storage periods than canned orange juices. This possibly indicated that furfural had little effect, if any, upon the flavor of canned citrus juices during storage.

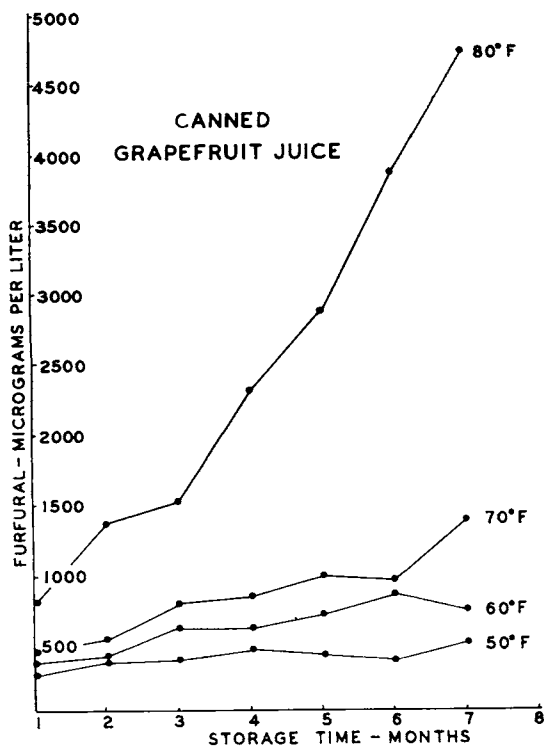


Fig. 4. Furfural content of canned grapefruit juice after storage at various temperatures.

Research studies since 1965. Since the investigation discussed in this paper was completed in 1965, additional papers have been published on the recovery of furfural from fresh and processed citrus juices, as well as the use of furfural as an index of flavor deterioration in processed citrus juices during storage. Comments on these more recent publications should be of merit.

Rymal *et al.* (11) reported that furfural rep-

Table 1. Flavor scores and average furfural in canned citrus juices after storage.

Average				
Flavor	7	6	5	4, 3
Score	Good	Fair	Fair	Poor
Juice	Furfural - averages ¹ micrograms/liter			
Hamlin	143	178	354	843
Valencia	131	201	593	1826
Grapefruit	296	481	751	2898

¹From 110 determinations.

Table 2. Correlation coefficients between furfural in canned citrus juices and flavor scores, storage temperatures and storage times.

	Citrus Juice		
	Hamlin	Valencia	Grapefruit
	Correlation coefficients (r)		
Flavor	-0.709**	-0.801**	-0.692**
Temp.	0.680**	0.702**	0.678**
Time	0.380*	0.383*	0.350*

* 5 percent level of significance.

** 1 percent level.

resented 12.8% of total volatiles recovered from canned orange juice stored at 80°F compared with less than 0.1% from that stored at 40°F, both having been stored for 27 months. Dinsmore and Nagy (4) did not detect furfural in either fresh orange juice or processed juice stored at 41°F. However, they reported that furfural was the most prominent volatile carbonyl compound captured from commercially glass-packed chilled orange juice that was stored in excess of 20 months at 86°F.

Dinsmore and Nagy (5) improved on the analytical procedures, used by Blair *et al.* (3), by using the more sensitive reaction of aniline and furfural and the more efficient rapid distillation procedure of Scott and Veldhuis (12). The authors agree that this is the preferred method for the determination of furfural. They also reported that when furfural was added to orange juice in the range of 200-2000 µg/liter, it was not detectable by a taste panel. Therefore, they stressed that furfural must be regarded only as an index of flavor deterioration during storage of canned citrus juices.

Nagy *et al.* (8) used furfural as an index of temperature abuse in commercially processed grapefruit juice, packed in cans and glass, and stored at temperatures of 40 to 85°F, inclusively. Nagy and Randall (9) made a similar study using commercially processed orange juice and later Dinsmore *et al.* (6) reported results from both of the previous investigations. All flavor evaluations were made using a triangular comparison test. Results indicated that the onset of flavor change occurs at a relatively low furfural level in a critical range of 50-70 µg/liter in orange juice and 155-200 µg/liter in grapefruit juice.

Thus the initial study in 1965 by Blair *et al.*

(3), reported in this current paper, stimulated interest in and led to an improved colorimetric method for furfural. Furfural content can be used as an index of flavor deterioration in processed citrus juices during storage.

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POTENTIAL BY-PRODUCTS FROM WASTE CITRUS PEEL EMULSION

W. L. BRYAN, O. W. BISSETT, C. J. WAGNER, JR.,
AND R. E. BERRY

Citrus and Subtropical Products Laboratory¹
Winter Haven

Abstract. Waste Valencia orange and grapefruit peel emulsions from citrus oil recovery units were evaluated as potentially valuable clouding agents for beverage concentrates where peel character might be desired. Initial cloud and cloud stability during extended centrifuging were similar to those for juices and pulp-wash suspensions. Cloud of orange emulsion which had been concentrated 20-fold, then reconstituted, was 70% of original; but ultrasonic treatment of concentrate increased this to about 80% by redispersing particle agglomerates. Twelve-fold grapefruit emulsion (3.5° Brix) retained more than 80% of initial cloud after reconstituting. Freezing the concentrates had no effect on cloud retention after reconstituting. Both concentrates retained some characteristic peel aroma and bitter flavor.

Introduction

For fruit drinks, demand for natural clouding agents, such as suspensions recovered from counter-current washing of pulp from juice finishers, has recently accelerated because of restrictions on use of brominated vegetable oil (BVO) in formulating cloud emulsions (8). The color and turbidity characteristics of waste citrus peel emulsions suggested their potential as natural clouding agents for fruit drink concentrates. This new use for waste peel emulsions might increase their value by opening new and more valuable markets, particularly in Europe.

Fruit drink concentrates made from whole fruit "squashes" have been popular for many years in Great Britain and Europe. They retain much of the characteristic aroma and taste of citrus peel. These concentrates contain at least 25% natural food parts, 80% of which may be peel constituents with very little juice (4). Such concentrates are somewhat bitter. They are generally stored unrefrigerated and prepared as drinks by mixing one part concentrate with three or four parts water. Thus, these reconstituted drinks generally contain 5 to 10% natural material derived from fruit.

Waste peel emulsions are available in quantity from two sources: 1) de-oiled waste effluent from d-limonene distillation units, and 2) centrifuge

¹One of the laboratories of the Southern Region, Agricultural Research Service, U. S. Department of Agriculture. References to specific commercial products do not constitute endorsement.

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