

Furfural Accumulation in Stored Orange Juice Concentrates

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The mode of furfural accumulation was determined in aseptically filled containers of single-strength orange juice and concentrates during storage at six different temperatures. Results showed that furfural accumulated in orange juice more rapidly than in concentrates of 34, 44, and 58 °Brix. There was 4 times the amount of furfural in orange juice (12 °Brix) than in concentrate (58 °Brix) stored at 17 °C for 100 days. A peak accumulation of furfural which was formed immediately after processing in high juice concentrates (58 °Brix) was eliminated by increasing deaeration. In concentrates evacuated to 40 mmHg, furfural concentration increased gradually during storage at a rate dependent on storage temperature and degree of juice concentration

Furfural has been recommended by several workers as an index of storage temperature abuse in commercially processed citrus juices (Dinsmore and Nagy, 1972; Maraulja et al., 1973; Nagy and Randall, 1973). Furfural in citrus juices seems to stem from the decomposition of ascorbic acid. However, it is well-known that furfural is also derived from the decomposition of pentoses and aldonic acids. Huelin (1953) found that furfural and CO₂ were the major decomposition products of 0.25% ascorbic acid in distilled water stored at 30 °C for 2 years. Studies by Tatum et al. (1969) on the nonenzymatic browning of orange powder showed that furfural formed during acid degradation of ascorbic acid. Finholt et al. (1965) found that the hydrogen ion catalyses anaerobic degradation of undissociated ascorbic acid and that furfural is formed at a rate equal to that of the disappearance of ascorbic acid.

Some of the pathways and reaction products which were postulated by Kurata and Sakurai (1967) showed that the steps of aerobic degradation of ascorbic acid are hydration of dehydroascorbic to ketogulonic acid, decarboxylation, and dehydration to furfural. The anaerobic degradation of ascorbic acid in acid conditions leads also to furfural and 3-deoxy-L-pentose as an intermediate.

A close correlation between furfural content and flavor changes has been demonstrated with grapefruit juice (Nagy et al., 1972; Maraulja et al., 1973) and orange juice (Nagy and Randall, 1973), but furfural per se does not have any flavor properties, even at a high concentration (Nagy and Randall, 1973).

The purpose of this study was to determine the mode of furfural accumulation in aseptically filled containers of orange juice and to compare it with concentrates, all stored at six different temperatures.

MATERIALS AND METHODS

Orange (var. Valencia) juice and concentrates of 34, 44, and 58 °Brix were produced in a line which comprised, in the order of the processed material's flow, the following units: industrial plate evaporator (A.P.V.); product pre-heater; vacuum deaerator; pasteurizer; product cooler; aseptic filling and seaming machine (Dole Model 1302, James Dole Corp., Redwood, CA). All heat exchangers were of the plate type. Aseptic conditions during filling and seaming were achieved in the Dole machine by superheated steam.

The following conditions existed along the material flow line: juice and concentrates were fed at 20 °C, preheated and allowed into the deaerator at 60 °C, deaerated at -720 nmHg (absolute pressure), pasteurized at 92-94 °C for 30 s, cooled and filled in cans at 35 °C, and sealed in cans and

cooled to 20 °C. All products were packed in 6-oz. cans, which were tin-plated, coated with lacquer, stored at -18, 5, 12, 17, 25, or 36 °C, and tested over a period of 18 months.

Furfural was determined by using an improved method of Dinsmore and Nagy (1974), based on the well-known aniline acetic acid reaction with furfural. The measurement of absorbance at 515 nm is specific for furfural. (Hydroxymethyl)furfural and methylfurfural absorb at different wavelengths and do not interfere with the results (Dunlop and Peters, 1953).

RESULTS AND DISCUSSION

Furfural accumulation occurred in all orange juices and concentrates stored at high temperatures. There was a very sharp accumulation of furfural in orange juice concentrates (58 °Brix) during the first days of storage, and very similar results were obtained during experiments with other varieties (Kanner et al., 1978), especially at 17 and 5 °C. After ~40 days the concentration of furfural dropped to a low level and once more accumulated in the product at a rate which was dependent on the storage temperature (Figure 1). The peak of furfural accumulation immediately after processing seems to coincide with the period at which ascorbic acid deteriorates aerobically.

This peak was eliminated in our recent experiments by increasing the deaerator unit and the vacuum from 140 to 40 mmHg (Figure 2). It was possible to reproduce the furfural peak by vigorous blending of the products with air before processing and by omitting the deaeration step (Figure 3).

Results showed that furfural increased in orange juice (11 °Brix) more rapidly than in juice concentrates of 34, 44, or 58 °Brix (Figures 4 and 5). Several research workers have shown that furfural is one of the main degradation products of ascorbic acid or dehydroascorbic acid (Huelin, 1953; Kurata and Sakurai, 1967; Tatum et al., 1969; Velisek et al., 1976). Ascorbic acid destruction in citrus products was found to be affected by the level of juice concentration (Curl, 1947; Kanner et al., 1978). This destruction in an orange juice concentrate of 58 °Brix, during storage for 200 days at 17 °C, was found to be twice that occurring in juice of 11 °Brix (Kanner et al., 1978). As furfural is a breakdown product from ascorbic acid, it was expected that a high amount of furfural would accumulate in products of high concentration. In fact, we found a 4-fold higher amount of furfural in juice of 11 °Brix than in orange concentrate of 58 °Brix (stored at 17 or 25 °C for 100 days) (Figure 5).

Furans and especially furfural and α,β -unsaturated aldehyde are known to be reactive compounds (Dunlop and Peters, 1953). Reactions of α -amino acids with furfural yielded pyrroles by a nucleophilic attack of the amines at the electrophilic position of the furan nucleus and alde-

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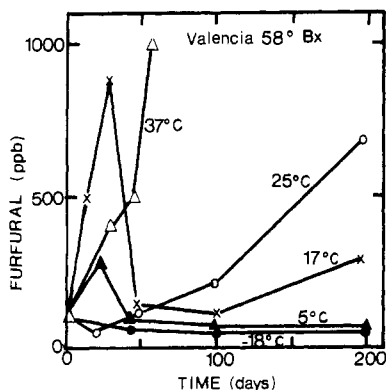


Figure 1. Furfural accumulation in Valencia concentrate (58 °Brix) as affected by storage temperature (vacuum of the deaerator was 140 mmHg). Values are the mean of three replications; significant difference at a level of 0.5 = 35 ppb. -18 (●); 5 (▲); 17 (×); 25 (○); 37 °C (△).

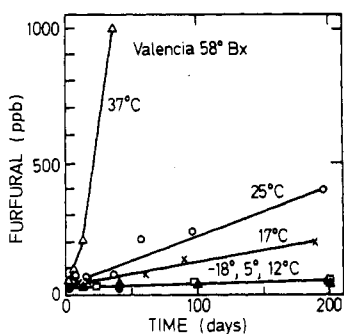


Figure 2. Furfural accumulation in Valencia concentrate (58 °Brix) as affected by storage temperature (vacuum of the deaerator was 40 mmHg). Values are the mean of three replications; significant difference at a level of 0.05 = 27 ppb.

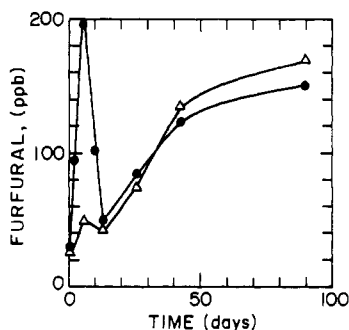


Figure 3. Furfural accumulation in Valencia concentrate (58 °Brix) stored at 25 °C as affected by deaeration. Values are the mean of three replications; significant difference at a level of 0.05 = 32 ppb. (▲) Without deaeration; (●) with deaeration.

mines by an attack of the amine on the aldehyde group (Rizzi, 1974). These reactions lead also to the development of strong colors and browning pigments (Burton et al., 1962; Clegg and Morton, 1965; Rizzi, 1974).

Our results indicate that the reaction between furfural and other compounds occurs at a high rate with increasing juice (compounds) concentration, and probably this is the reason why less furfural accumulated in concentrates than in juice. A rapid decomposition of furfural was demonstrated in 58 °Brix inferior deaerated concentrates (Figures 1 and 3).

In juice, the accumulation of furfural is higher than its decomposition, so in this product furfural can serve as a quality deterioration index, as has been recommended by several workers (Maraulja et al., 1973; Nagy et al., 1972; Nagy and Randall, 1973).

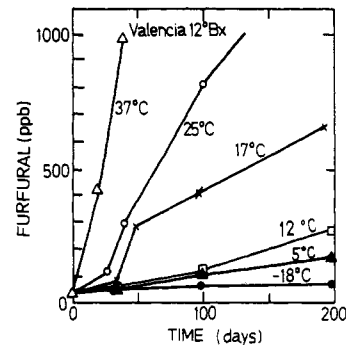


Figure 4. Furfural accumulation in Valencia juice (12 °Brix) as affected by storage temperature (vacuum of the deaerator was 40 mmHg). Values are the mean of three replications; significant difference at a level of 0.05 = 21 ppb.

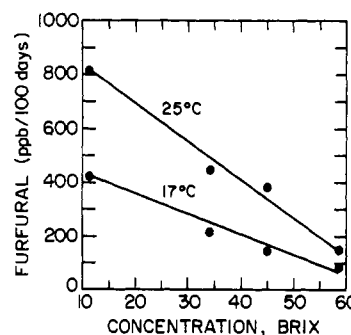


Figure 5. Effect of juice concentration on furfural accumulation.

As furfural generates and decomposes simultaneously in orange concentrates, it would be more difficult to use it as an index for predicting product quality changes. However, when concentrates were evacuated to 40 mmHg, the furfural levels increased gradually during storage, at a rate which was specific for each degree of juice concentration. Studying carefully this rate of furfural accumulation could indeed predict storage temperature abuse in orange juice concentrates

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