sons data. However, there are some interesting trends which appear in the data. Percent centrifuged pulp averages were lower in the juice centrifuged hot in both the Hamlin and Pineapple orange juices. Total glycosides were over 8% higher in Pineapple orange juice centrifuged hot. The color number was lower in all three varieties in the hot juice. These observations are only trends as there was not any statistical significance ($P < 0.05$) determined.

During the course of the project, several minor problems were encountered in the operation of the centrifuge which may have had a bearing on its efficiency. These problems and possible solutions were previously reported (2).

In conclusion, only the % Light Transmission reading from Valencia orange juice showed statistical significance ($P < 0.05$) between juice centrifuged at ambient and at 195°F, on a seasonal and combined seasons basis. Significant differences ($P < 0.05$) were also found in the percent centrifuged pulp content and percent oil content of Pineapple orange juice on a seasonal basis but not on a combined seasons basis. These small differences support the use of a centrifuge in connection with equipment which produce a hot juice (such as between the stages of an evaporator) in order to increase equipment efficiency and/or product quality.

### Literature Cited


1. Attaway, A. J., et al. 1972. Some new analytical indicators of processed orange juice quality. 1971-72. Proc. Fla. State Hort. Soc. 85:192-202.
2. Barros, S. M. 1989. Effects of temperature on pulp removal from orange juice by centrifugation. Proc. Fla. State Hort. Soc. 102:152-154.
3. Barros, S. M., Davis, J. E., and Fellers, P. J. 1986. Effects of simulated bin storage on the juice quality and yield of freeze-damaged Valencia oranges. Proc. Fla. State Hort. Soc. 99:103-105.
4. Fellers, P. J. and Barron, R. W. 1987. A commercial method for recovery of natural pigment granules from citrus juices for color enhancement purposes. J. Food Sci. 52:994-995, 1005.
5. Mannheim, C. H. and Passy, N. 1977. Recovery and concentration of citrus aroma. Proc. Int. Soc. Citriculture. 3:756-762.
6. Moore, E. L., Atkins, C. D. and Wiederhold, E. 1948. A progress report on Persian limes. Citrus Ind. 29(6):5-6.
7. Murdock, D. I. 1977. Microbiology of citrus products. In *Citrus Science and Technology*, Vol. 2 (Ed.) S. Nagy, P. E. Shaw, and M. K. Veldhuis. AVI Publishing Co., Inc., Westport, CT.
8. Peleg, M. and Mannheim, C. H. 1970. Production of frozen orange juice concentrate from centrifugally separated serum and pulp. J. Food Sci. 35:649-651.


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# NONENZYMIC BROWNING AND CORROSION IN STORED SINGLE-STRENGTH GRAPEFRUIT JUICE


STEVEN NAGY, SEIFOLLAH NIKDEL AND MARTIN KLIM
*Scientific Research Department*
*Florida Department of Citrus*
*700 Experiment Station Road*
*Lake Alfred, Florida 33850*



*Abstract.* **Nonenzymic browning and corrosion were monitored in commercially canned single-strength grapefruit juice stored for 15 weeks at 10°, 20°, 30°, 40°, and 50°C. Browning did not occur in juices stored at 10° and 20°C, but began to appear after 9 weeks in juices stored at 30°C. Browning was quite evident within 3 weeks for juices stored at 40° and 50°C. Plots of nonenzymic browning versus corrosion (tin and iron dissolution) showed significant correlations and equations that best fit these correlations were quadratic. At high storage temperatures, the protection exerted by tin against nonenzymic browning is diminished and juice discoloration was evident. Possible hypotheses for the protective effects of tin are presented. When the dissolved tin level exceeded about 60 mg tin/kg juice, noticeable browning occurred. The iron level of juice does not appear to manifest protective activity and, in fact, might be detrimental.**


Color is an important quality factor in the marketing of citrus juices. Change in color, primarily manifested by nonenzymic browning, reduces consumer acceptance and, therefore, is an important shelf-life variable. Although significant differences in brown pigment formation appear more dependent on thermal processing and storage (6), the type of packaging container contributes to hue changes and the overall brown perception of the product (3). Nonenzymic browning develops faster and more intensely in glass-packed juices than in juices packed in tinplate containers (10, 17).

Packaging of citrus juices in tinplate containers offers many advantages over other types containers (glass, fiberboard, plastic, aseptic packages), namely, ease of packing, sterilizing, handling and transporting. However, a major disadvantage in the use of tinplate cans is potential corrosion. During the corrosion process, metallic off-flavors are introduced into the product and notable amounts of tin and iron are dissolved by the acidic juice. Extensive studies have been conducted to evaluate the influence of temperature and storage time on corrosion in processed canned citrus juices (9, 11, 12, 18). However, no reported studies have been conducted on the relationship of nonenzymic browning to the dissolution of tin and iron during storage of processed canned citrus juices. To this end, we report the results of our investigations on reaction rate kinetics of nonenzymic browning and corrosion in canned single-strength grapefruit juice.

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### Materials and Methods

*Samples and Storage Treatments.* Commercially processed single-strength grapefruit juice (SSGJ) was purchased from a local processing company. All samples were produced from the same batch of reconstituted concentrate, and were packed in tinplated cans with enamel-coated lids (177 ml; 48 cans per case). All samples were obtained during the time of processing and immediately transported to the Citrus Research and Education Center. Canned SSGJ were placed in storage lockers (about 100 cans) at varying temperatures, namely, 10°, 20°, 30°, 40° and 50°C and stored for 3, 6, 9, 12, and 15 weeks. Three cases of grapefruit juice were placed at −22°C and were considered as "nontreated samples" (controls). Samples were randomly selected at specific time periods and analyzed for nonenzymic browning, and tin and iron contents.

*Browning Determination.* Nonenzymic browning of SSGJ was determined by an improved method of Klim and Nagy (2) with slight modifications (10). Clarified, filtered samples were read at 420 nm with a single-beam Bausch and Lomb Spectronic 88 using 13-mm cuvettes (10-mm light path). The analog signal from the spectrometer was measured with a Fluke Model 75 3½-digit multimeter for improved accuracy. Readings were recorded to three significant figures. Absorbances of samples subjected to different storage temperatures and times were reported as absorbance difference data by subtracting the treated sample absorbance from freshly canned juice absorbance, namely,

$$\Delta A_{420} = A_{420} \text{ treated sample} - A_{420} \text{ nontreated sample}$$

*Iron and Tin Measurements.* Minerals in SSGJ were determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES). The SSGJ sample was accurately weighed (12 to 12.5 g) into a Teflon digestion vessel (MDS-81D; CEM Co., Indian Trail, NC). To this sample was added 1.25 g conc. $HNO_3$, 3.75 g conc. HCI and the mixture brought accurately to a total weight of 25 g with deionized water. The Teflon vessel, containing a 7.03 kg/$cm^2$ pressure relief valve and threaded cap, was closed with a CEM capper. The vessel was placed in a programmable 600 W microwave oven with rotating turntable and programmed for 8 min at 100% power, then left for 5 min at 0% power and, finally, 8 min at 100% power. The digestion vessel was cooled to room temperature, opened using the capping station, and the contents filtered through ashless filter paper (Whatman #42). Digestion of SSGJ samples in an enclosed Teflon vessel by microwave resulted in recoveries of greater than 99% for Sn and Fe as evidenced by ICP analyses. Samples were stored in polyethylene or Teflon bottles pending analyses. Spectrochemical analysis was carried out with a Jarrel-Ash Atomscan 2000 sequential and computer-controlled spectrometer equipped with an autosampler. Sample gas flow determines the velocity of argon through the nebulizer and was set to 0.6 L/min for high power (1.4-1.5 kw). The observation height was 16 mm above the coil. Sample uptake rate was 1 ml/min and the spectral resolution was 0.018 nm for 178-380 nm and 0.036 nm for 380-780 nm. Analytical lines used for these analyses were 238.20 nm (Fe) and 235.48 nm (Sn).

*Other Methods.* Degrees Brix, percent citric acid and pH were determined by recognized analytical methods (15). Statistical evaluation of data was conducted with the SAS PC Version 6.03 (SAS Institute, Inc., Cary, NC).

## Results and Discussion

The processed SSGJ employed in these studies possessed the following properties: 10.2° Brix, 1.11% citric acid, pH 3.36, Brix/acid ratio 9.2. The tin and iron contents of these freshly canned samples averaged 17 mg/kg and 1.7 mg/kg, respectively. Mineral contents of these commercial grapefruit juices prior to canning were not ascertained because of flow throughput processes within a closed system during processing and canning. Nikdel (1985), however, reported tin contents of freshly prepared grapefruit juices (noncanned) to be below the detection limit of the ICP-AES, namely, less than 0.030 mg/kg. The process of packing hot juice into a tinplated can cause immediate dissolution of the tin coating and, hence, the reason why a freshly packed product contains high levels of tin. Factors responsible for these elevated levels were enumerated by Nagy et al. (12) and by Rouseff and Ting (19). Nagy (8) reported iron contents of noncanned SSGJ to range between 0.6 and 1.9 mg/kg. The initial level of iron found in these samples (1.7 mg/kg) indicated that there was minimal dissolution of the base plate during canning. However, iron does dissolve from the base plate during elevated temperature storage of canned juices (9).

Nonenzymic browning index values for SSGJ's were obtained by measuring absorbance at 420 nm and correcting those values by subtracting from the absorbance value of nontreated processed juice. Nontreated canned SSGJ yielded an average $A_{420}$ of 0.104 (CV = 2.9%). The corrected absorbance values ($\Delta A_{420}$) are considered a reasonably true measure of browning changes occurring during storage. Table 1 lists the mean browning index values of SSGJ stored for varying periods and temperatures. As noted by Table 1, minimal browning change occurs in juices stored at 10° and 20°C (nonsignificant, $p > .05$). With 30°C-stored juices, noticeable changes were evident after the 9th week ($p < .01$). Major changes in browning occurred at the higher storage temperatures, namely, 40° and 50°C ($p < .01$).

The relationship of corrosion (tin and iron dissolution) and nonenzymic browning has never been ascertained. Concurrent examination of corrosion and nonenzymic browning in randomly selected samples yielded data shown in Figures 1 and 2. As noted in Figure 1, tin dissolution versus nonenzymic browning, the equation which best represents this relationship is second order with respect to tin conc. ($y = a + bx + cx^2$). The regression equation is $y = -0.0091 + 0.000159\,x + .000009x^2$ where x = mg tin/kg juice ($R^2 = .973$). The equation and model indicate a high correlation (relationship) between detinning of the can and increase in nonenzymic browning absorbance. The data indicates that nonenzymic browning begins to increase when the level of dissolved tin exceeds about 60 mg/kg juice.

Figure 2 shows nonenzymic browning absorbance changes versus juice iron contents. The best-fit equation is also quadratic but the correlation ($R^2 = .769$) is not as high

Table 1. Mean browning index values ($\Delta A_{420}$) of canned SSGJ stored at varying temperatures and storage times.

| | Temp. (C) | | | | |
|---|---|---|---|---|---|
| Time (wk) | 10 | 20 | 30 | 40 | 50 |
| 3 | .005 | .002 | .002 | .032 | .088 |
| 6 | .005 | .005 | .008 | .061 | .185 |
| 9 | .003 | .005 | .009 | .132 | 2.83 |
| 12 | .007 | .003 | .024 | .212 | .415 |
| 15 | .006 | .009 | .022 | .290 | .529 |
| $R^2$ | .007 | .002 | .709 | .974 | .990 |
| significance | NS | NS | .01 | .01 | .01 |

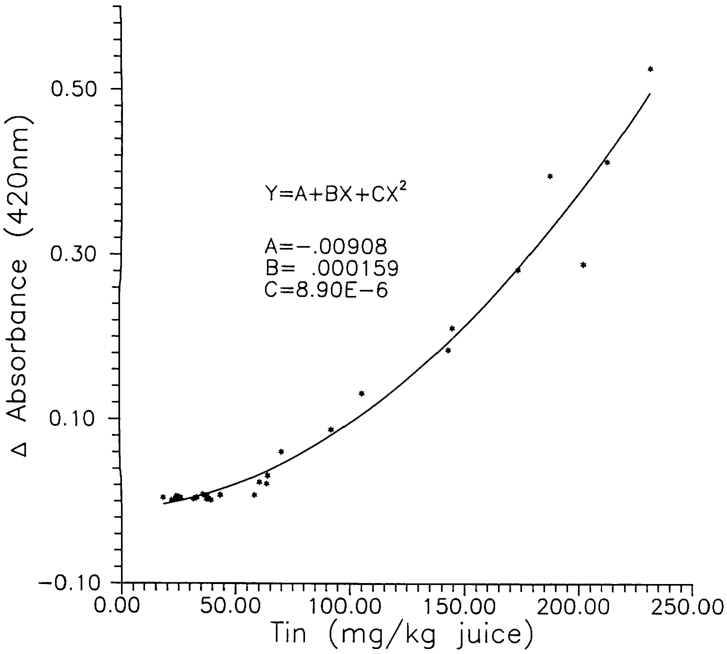


Fig. 1. Browning changes ($\Delta A_{420}$) versus tin contents.

as tin. The iron level of juice does not appear to exert protection against nonenzymic browning and, in fact, might be detrimental.

SSGJ, when packed in cans, is subject to less nonenzymic browning when contrasted to other type containers (5, 6, 10, 17). The tinplate inhibits vitamin C breakdown (7, 12) and furfural accumulation; both factors of which have been strongly implicated in nonenzymic browning (4, 7). Major disadvantages of canned juice products, however, are corrosion and the introduction of metallic off-flavors.

The protection exerted by tin against nonenzymic browning is related to its favorable oxidation-reduction (redox) potential and, secondly, to its ionic-binding ability. In freshly processed juice, oxygen is dissolved in the juice and entrapped within the can headspace. Dissolution of the tinplate through oxidation reduces oxygen which might otherwise enter into detrimental reactions, e.g., peroxide formation. The redox mechanism is:

$$SN^\circ \rightarrow Sn^{++} + 2e^- \qquad E^\circ = +0.136$$
$$0_2 + 4H^+ + 4e^- \rightarrow 2H_20 \qquad E^\circ = +1.467$$
$$2Sn^\circ + 0_2 + 4H^+ \longleftrightarrow 2Sn^{++} + 2H_2O \qquad E^\circ = +1.467$$
$$\Delta G^\circ = -566 \text{ K Joules/mol}$$

Iron is a metal that is present in citrus juice at levels of 0.6 to 1.9 mg/kg (8, 14) and manifests catalytic activity in lipid oxidation and vitamin C degradation (20). The fact that vitamin C degradation is strongly implicated in nonenzymic browning of citrus juices (4,6) adds importance to the juice's iron level. Examination of the redox reaction of iron and tin reinforces the protective action of tin, namely,

$$Sn^\circ \rightarrow Sn^{++} + 2e^- \qquad E^\circ = +0.136$$
$$2Fe^{+++} + 2e^- \longleftrightarrow 2Fe^{++} \qquad E^\circ = +0.770$$
$$SN^\circ + 2Fe^{+++} \longleftrightarrow Sn^{++} + 2Fe^{++} \qquad E^\circ = +0.906$$
$$\Delta G^\circ = -174 \text{ K Joules/mol}$$

Rezaaiyan and Nikdel (16) studied the valence state of tin in single-strength citrus juices packed in tinplated cans. After tin reacted and dissolved in the juice, Rezaaiyan and Nikdel (16) observed both valence states of $Sn^{+2}$ and $Sn^{+4}$. In addition to its strong antioxidant activity, tin is also an effective chelating metal (log $K_f$ = 18.3; EDTA) (1). Since carbonyl compounds are important intermediates during nonenzymic browning of citrus juices (4), the presence of a chelating metal ($Sn^{+2}$; $Sn^{+4}$) to bind to reactive carbonyls might be one reasonable explanation for the suppression of nonenzymic browning in tinplated, canned citrus juices as observed earlier (4, 6, 10, 17).

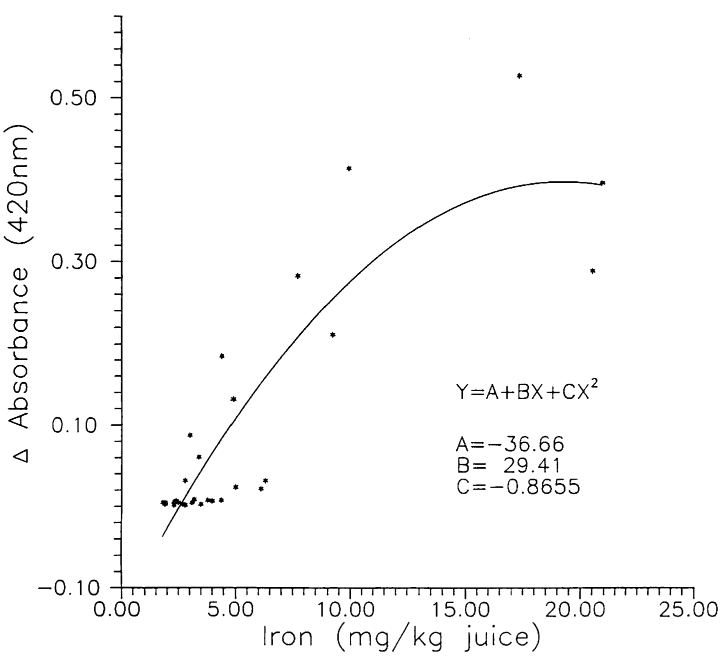


Fig. 2. Browning changes ($\Delta A_{420}$) versus iron contents.

## References


1. Harris, D. C. 1987. Quantitative Chemical Analysis. 278. W. H. Freeman and Co., New York.
2. Klim, M. and Nagy, S. 1988. An improved method to determine nonenzymic browning in citrus juices. J. Agric. Food Chem. 36:1271-1274.
3. Lee, H. S. and Nagy, S. 1988. Measurement of color changes due to browning in stored grapefruit juices. Proc. Fla. Hort. Soc. 101:154-157.
4. Lee, H. S. and Nagy, S. 1988. Quality changes and nonenzymic browning intermediates in grapefruit juice during storage. J. Food Sci. 53:168-172, 180.
5. Lopez, A. 1987. A Complete Course in Canning, Book II. Chapter 2. The Canning Trade, Inc., Baltimore, MD.
6. Marshall, M., Nagy, S. and Rouseff, R. 1986. Factors impacting on the quality of stored citrus fruit beverages. In: G. Charalambous (ed.) The Shelf Life of Foods and Beverages. 237-254. Elsevier Science Publishers, Amsterdam.
7. Moore, E. L., Esselen, W. F. and Fellers, C. R. 1942. Causes of darkening of packaged orange juice. The Canner. 95:11-13.
8. Nagy, S. 1977. Inorganic elements. In: S. Nagy, P. E. Shaw, M. K. Veldhuis (eds.). Citrus Science and Technology, Vol. 1. 479-495. AVI Publishing Co., Westport, CT.
9. Nagy, S. and Nikdel, S. 1986. Tin, iron, and alumnium contents of commercially canned single-strength grapefruit juice stored at varying temperatures. J. Agric. Food Chem. 34:588-593.
10. Nagy, S., Lee, H., Rouseff, R. L. and Lin, J.C.C. 1990. Nonenzymic browning of commercially canned and bottled grapefruit juice. J. Agric. Food Chem. 38:343-346.

11. Nagy, S. and Rouseff, R. L. 1981. Lead contents of commercially canned single-strength orange juice stored at various temperatures. J. Agric. Food Chem. 29:889-890.
12. Nagy, S., Rouseff, R. L. and Ting, S. V. 1980. Effects of temperature and storage on the iron and tin contents of commercially canned single-strength orange juice. J. Agric. Food Chem. 28:1166-1169.
13. Nikdel, S. 1985. Unpublished results. Florida Department of Citrus, Lake Alfred.
14. Nikdel, S., Rouseff, R. and Fisher, J. 1987. Comparative effects of three types of Florasil treatments on flavanone glycosides and minerals of processed grapefruit juice. J. Food Sci. 52:1673-1675.
15. Redd, J. B., Hendrix, C. M., and Hendrix, D. L. 1986. Quality Control Manual for Citrus Processing Plants. Intercit, Inc., Safety Harbor, Florida.
16. Rezaaiyan, R. and Nikdel, S. 1988. Unpublished results. Florida Department of Citrus.
17. Rouseff, R. L., Fisher, J. F. and Nagy, S. 1989. HPLC separation and comparison of the browning pigments formed in grapefruit juice stored in glass and cans. J. Agric. Food Chem. 37:765-769.
18. Rouseff, R. L. and Ting, S. V. 1980. Lead uptake of grapefruit juices stored in cans as determined by flameless atomic absorption spectroscopy. J. Food Sci. 45:965-968.
19. Rouseff, R. L. and Ting, S. V. 1985. Effects of pH, storage time and temperature on the tin content of canned single-strength grapefruit juice. J. Food Sci. 50:333-339.
20. Tannenbaum, S. R., Young, V. R. and Arden, M. C. 1985. Vitamins and minerals. In: O. R. Fennema (ed.). Food Chemistry. 477-544. Marcel Dekker, Inc., New York.

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# PRODUCTION AND CHARACTERIZATION OF CARAMBOLA ESSENCE

STEVEN NAGY, SANTIAGO BARROS, AND ROBERT CARTER
[1]*Scientific Research Department*
*Florida Department of Citrus*
*700 Experiment Station Road*
*Lake Alfred, Florida 33850*

AND

CHIN SHU CHEN
*University of Florida, IFAS*
*Citrus Research and Education Center*
*700 Experiment Station Road*
*Lake Alfred, Florida 33850*

*Abstract.* **The carambola (*Averrhoa carambola* L. cv. Arkin), also known as star fruit, was obtained from a South Florida packinghouse, and the juice extracted with an FMC citric juice finisher. The juice was then concentrated to 62° Brix using a 3-effect, 4-stage pilot-plant TASTE citrus evaporator equipped with an essence recovery unit. The recovered essence possessed an unripe apple-like or apricot-like aroma note. Carambola essense was examined by gas chromatography-mass spectrometry and revealed ethyl acetate, *trans*-2-hexenal, *cis*-3-hexenol, *trans*-2-hexenol, n-hexanol and several minor alchols, esters and terpenes. The pleasant aromatic property of carambola essense suggests potential commercial utilization in fruit juices and drinks.**

The carambola (*Averrhoa carambola* L.), also known as star fruit and other names specific to different geographic locations, is thought to have originated in Sri Lanka and the Moluccas (7). The fruit is ovoid to ellipsoid, 6-15 cm in length, with 5 (rarely 4 or 6) prominent longitudinal ribs, and star-shaped in cross section. The flesh is light yellow to yellow, translucent and very juicy. Wagner et al. (11) reported ascorbic and oxalic acid contents, acidity, Brix, and taste panel evaluation for carambolas that were mostly of the yellow varieties. Campbell et al. (3) reported postharvest changes in color and compositional characteristics (soluble sugars, organic acids) in 'Arkin' and 'Golden Star' carambolas.

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The flavor of carambola is variable, and ranges from sour with little sugar to sweet with little acid (4, 11). Few studies on the identity and quantitative approximation of volatile flavor components of carambolas have been reported (12). Siota (10) and Wilson et al. (13) reported GLC area percentages for volatile components from solvent extracts of carambola purees. In the study by Wilson et al. (13), 43 volatiles were enumerated, namely, 13 alcohols, 4 aldehydes, 6 ketones, 13 esters, 3 hydrocarbons and 4 compounds classified as miscellaneous.

In this study, an attempt was made to evaluate the adaptation of commercial citrus processing equipment for potential application in tropical fruit processing. We report for the first time, the volatile composition and aroma quality of carambola essence prepared by a 3-effect, 4-stage TASTE citrus evaporator. This study should enhance our knowledge for potential commercialization of carambola products, especially carambola essense and juice.

## Materials and Methods

*Samples.* Ripe carambolas (cv. 'Arkin') were obtained from a major South Florida packinghouse (J. R. Brooks and Sons, Homestead) and transported to the Citrus Research and Education Center, Lake Alfred, FL. The fruit were stored at 40°F until processing.

*Processing.* The juice was extracted from the fruit at about 40°F using a screw-type finisher (FMC Model 35 finisher with reinforced .027 finisher screen openings). The juice was then concentrated to 62°Brix. The carambola concentrate was produced using a 3-effect, 4-stage TASTE citrus evaporator capable of evaporating 500 lbs of water per hour (5, 8). The TASTE citrus evaporator was equipped with an essence recovery system that recovered the carambola essence (2). The TASTE citrus evaporator was designed to pasteurize juice at about 212°F for 10 sec, which is sufficient for most fruit juice processing.

*Essence Analyses.* Samples were chromatographed on a Hewlett-Packard Model 5890 gas chromatograph fitted with a 0.32 mm i.d. x 30 m bonded-phase, nonpolar RTX-5 fused silica capillary column (film thickness 1 micron) (Restek Corp., Bellefonte, PA). Operational parameters included: injection port and flame ionization detector set at 240°C and 250°C, respectively. The carrier gas (hydrogen)