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Nonenzymic Browning of Commercially Canned and Bottled Grapefruit Juice

Steven Nagy,*,† Hyoung Lee,† Russell L. Rouseff,‡ and James C. C. Lin†

Scientific Research Department, Florida Department of Citrus, 700 Experiment Station Road, Lake Alfred, Florida 33850, and Citrus Research and Education Center, University of Florida, 700 Experiment Station Road, Lake Alfred, Florida 33850

Nonenzymic browning was monitored in canned and bottled single-strength grapefruit juice stored at 10–50 °C over an 18-week period. Browning occurred faster and developed more intensely in bottled juices than in canned juices. No browning occurred in canned juices stored at 10 and 20 °C. Regression analyses of juices stored at 40 and 50 °C yielded complex polynomial models to statistically define the nonenzymic browning profiles. The apparent rates of reaction at those temperatures were nonuniform over time. Simplistic zero- or first-order models should not be used to define nonenzymic browning of citrus juices at storage temperatures exceeding 30 °C.

Nonenzymic browning is a major factor in quality loss of processed citrus juices. Although extensive studies (Nomura, 1955; Joslyn, 1957; Clegg and Morton, 1965; Wolfrom et al., 1974; Meydav and Berk, 1978; Lee and Nagy, 1988a,b) have been conducted on elucidating browning precursors and reaction conditions, the chemical pathways to pigment formation are not entirely understood. Recently, HPLC separation and UV–vis spectral characterization of brown pigments in aged citrus juice revealed complex patterns that changed with time, temperature, and packaging container (Rouseff et al., 1987, 1989). Those studies revealed that greater numbers of browning pigments were formed in bottles than in cans and fewer but more intense browning pigments were formed in cans. Some brown pigments were unstable and diminished or disappeared with extended storage time, whereas others increased with increasing time. Although significant differences in brown pigment formation appear more dependent on thermal processing and storage (Marshall et al., 1986), the type of packaging container contributes to hue changes and the overall brown perception of the product (Lee and Nagy, 1988c).

Many nonenzymic browning studies have been conducted with model citrus systems, but limited data are available on authentic commercial citrus juices (Saguy et al., 1978; Passy and Mannheim, 1979). Kinetic studies on the browning of grapefruit juice (Passy and Mannheim, 1979) showed that the reaction first proceeded through a lag period where minimal changes in absorbance (420 nm) occurred and, then, was followed by a postlag period of rapidly changing absorbance. Many workers (Joslyn, 1957; Clegg and Morton, 1965; Lee and Nagy, 1988b) have concluded that the lag period constitutes the time interval wherein colorless, browning precursors form. Brown pigment formation occurs during the postlag period and is dependent on many factors, namely, soluble solids, ascorbic acid, pH, oxygen level, metal ions, packaging container type, and temperature (Karel and Nickerson, 1964; Saguy et al., 1978; Robertson and Reeves, 1981; Lee and Nagy, 1988c).

The objectives of the current study were to monitor the development of browning in commercially processed single-strength grapefruit juice packaged in cans and bottles by a sensitive index of nonenzymic browning (Klim and Nagy, 1988) and to develop empirical (predictive) equations to define the rates of reaction as affected by storage temperatures and container type.

† Florida Department of Citrus.
‡ University of Florida.

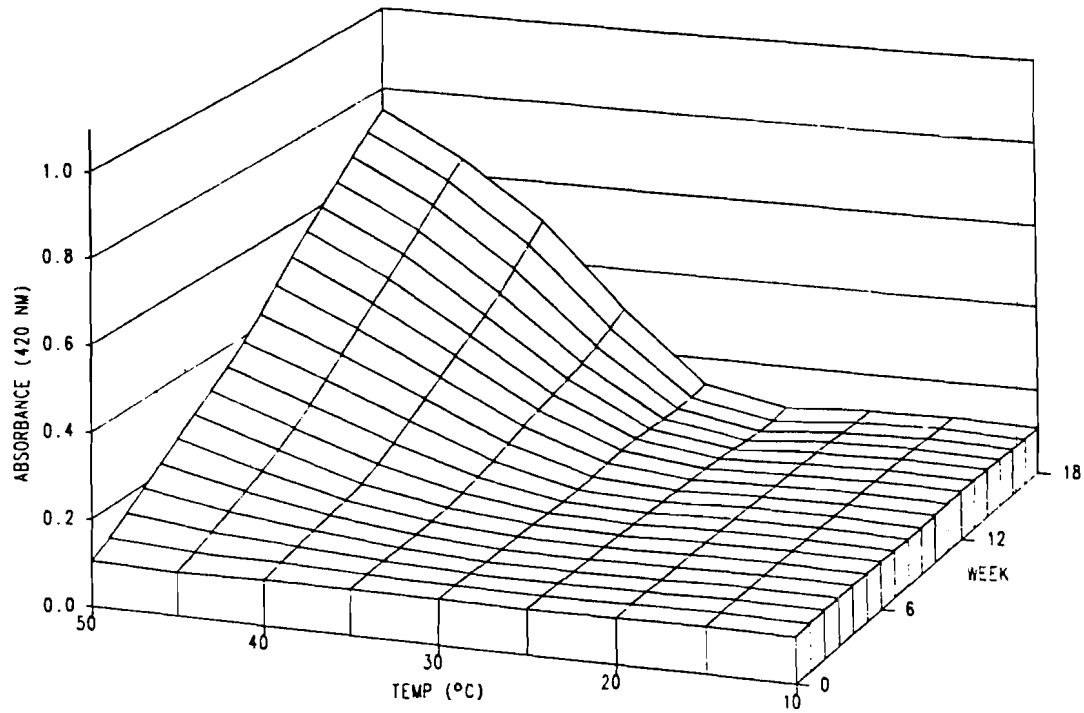

Figure 1. Three-dimensional plot of nonenzymic browning (A_{420nm}) of canned grapefruit juice versus storage temperatures and weeks.

EXPERIMENTAL SECTION

Samples. Commercially processed single-strength grapefruit juices were purchased from a local processing company. Grapefruit samples were packed in tin-plated cans with enamel-coated lids (177 mL; 48 cans/case) and glass bottles (208 mL; 24 bottles/case). Samples were obtained during the time of production and placed in a refrigerated storage at 5 °C. Both the canned and bottled juices were reconstituted from concentrate from lots prepared 1 week apart.

Browning Determination. Browning of grapefruit juice samples was determined by a method similar to that of Klim and Nagy (1988) with an additional membrane filtration step. The method entailed the following steps:

Step 1. Ten milliliters of single-strength grapefruit juice was centrifuged at 1000*g* for 15 min.

Step 2. Three milliliters of the supernatant fluid was removed and placed in a 10-mL centrifuge tube. Three milliliters of methanol was added and the solution mixed and placed in an ice bath for 15 min to accelerate flocculation of finely suspended, colloidal particles.

Step 3. The sample was recentrifuged at 1000*g* for 15 min and the supernatant fluid removed and passed through a 0.45-μm 13-mm disposable syringe filter (Nylon Acrodisc 13; Gelman Sciences).

Step 4. The clear solution was read at 420 nm (browning index) with a Bausch and Lomb Spectronic 88 using 13-mm cuvettes (10-mm light path).

Other Methods. Degrees Brix, percent citric acid, and pH were determined by recognized analytical methods (Redd et al., 1986). Statistical evaluation of data was conducted with the SAS PC Version 6.03 (SAS Institute, Inc., Cary, NC).

Experimental Design. A total of 144 canned samples and 72 bottled samples were placed in each of five storage lockers at 10, 20, 30, 40, and 50 °C. The total number of samples was 720 cans and 360 bottles. At 3-week intervals for a total of 18 weeks, 10 cans and 10 bottles were randomly removed from each storage locker. From the 10 samples, 3 were taken for browning determinations and the remaining were placed in cold storage for further studies or additional replication.

RESULTS AND DISCUSSION

The processed grapefruit juices used in these studies possessed the following properties: (A) canned, 10.3° Brix, 1.12% citric acid, pH 3.36, Brix/acid ratio 9.2; (B) bottled, 9.9° Brix, 0.99% citric acid, pH 3.48, Brix/acid ratio 10.

Figures 1 and 2 depict the three-dimensional relationship of browning (absorbance at 420 nm) versus storage temperatures and weeks for canned and bottled grapefruit juices. Over the 18-week period, minimal browning occurred during storage at 10 and 20 °C for both canned and bottled juices. Storage temperatures of 30–50 °C resulted in rapid increases in browning. Bottled juices showed faster and greater changes in absorbance than the canned juices. Since compositional properties of the bottled and canned juices were similar, differences in absorbance were primarily attributed to the packaging container.

Regression plots from statistical evaluation by SAS of the data from the five storage temperatures for canned and bottled juices are shown in Figures 3 and 4, respectively. Table I summarizes the regression equations for best curve fitting for the canned and bottled juices. For canned juices stored at 10 and 20 °C, no significant change in absorbance versus time over the 18-week period was observed as evidenced by a virtual zero slope. Absorbance (Y) is essentially equal to a constant (C); i.e., $Y = C$. Canned juice stored at 30 °C yielded a linear plot (straight line), whereas nonlinear relationships were evident with 40 and 50 °C stored juices. Equations that best fit the 40 and 50 °C juices contained statistical quadratic functions (x^2) and, thus, yielded curved lines (Figure 3).

Passy and Mannheim (1979) studied browning in canned concentrated grapefruit juice (60° Brix) and defined a lag period (time of nonchanging absorbance) and a post-lag period (time of rapid changing absorbance. The post-lag period was denoted by a linear increase in absorbance that Passy and Mannheim (1979) defined as obeying zero-order kinetics. In our studies with canned single-strength juice (10.3° Brix), we could not clearly identify a lag period, especially for the 40 and 50 °C stored juices.

Browning occurs much faster with concentrated juice

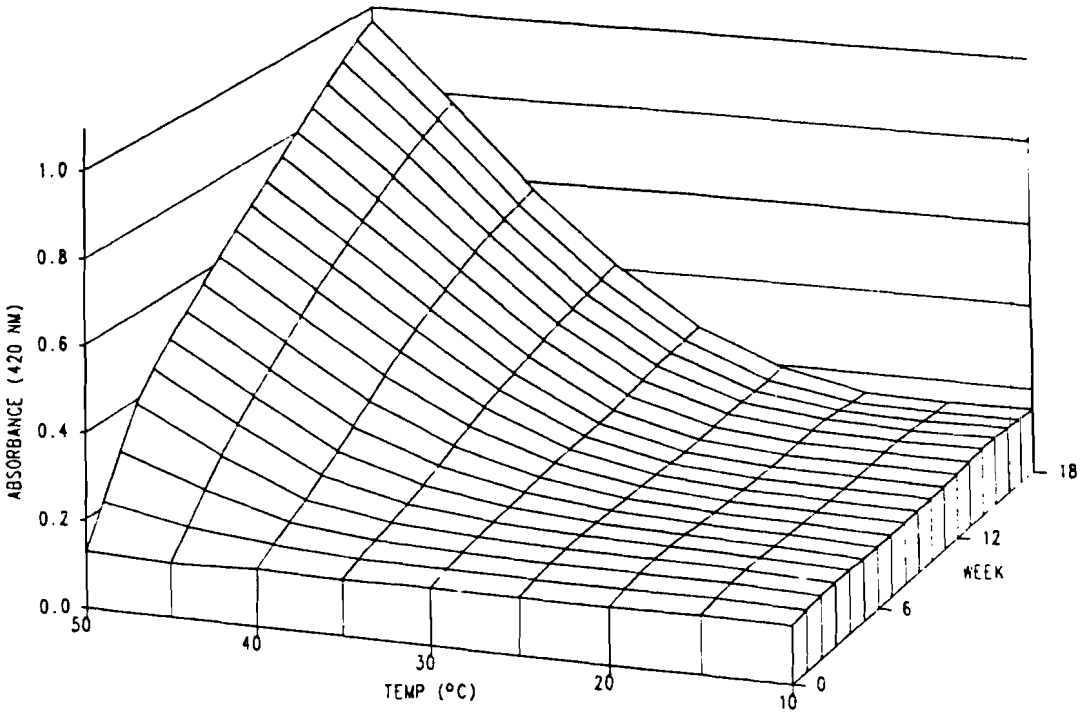

Figure 2. Three-dimensional plot of nonenzymic browning (A_{420nm}) of bottled grapefruit juice versus storage temperatures and weeks.

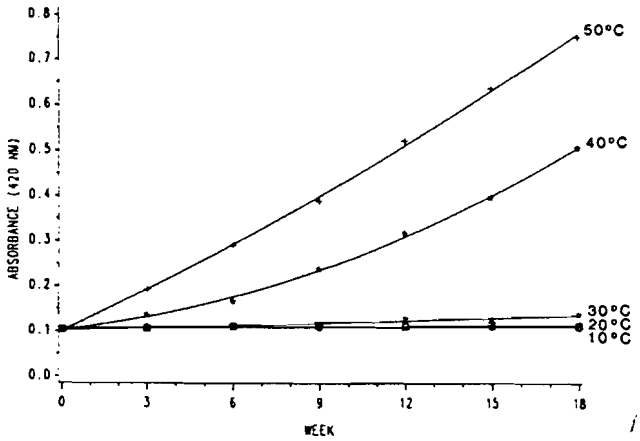

Figure 3. Regression analyses of nonenzymic browning (A_{420nm})of canned grapefruit juice stored at 10–50 °C.

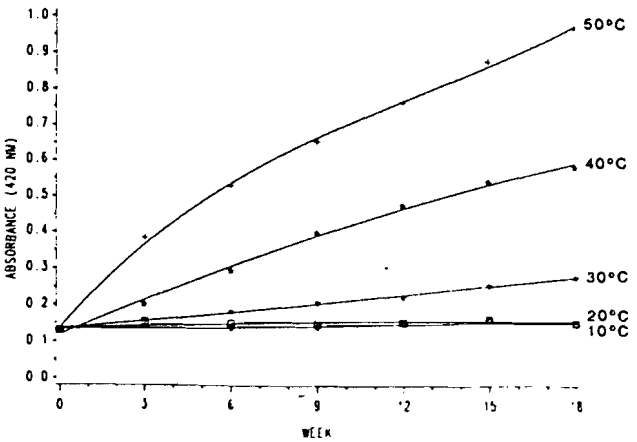

Figure 4. Regression analyses of nonenzymic browning (A_{420nm}) of bottled grapefruit juice stored at 10–50 °C.

than single-strength juice. The greater the concentration (as measured by degrees Brix), the faster the rates

ner et al., 1981, 1982; Malone, 1984). Apparently, with concentrated juice, change from lag period to postlag period is more readily perceived.

Figure 4 and Table I indicate faster and more extensive browning changes for bottled grapefruit juice versus canned juices. These observations are in keeping with our previously published studies on other degradative changes showing that furfural accumulation (Nagy et al., 1972), vitamin C breakdown (Nagy, 1980), and flavor changes (Nagy and Rouseff, 1980) occurred much faster in bottled citrus juices than in similar canned products. In contrast to canned juices, bottled juices stored at 10 and 20 °C showed increasing absorbance changes over time best described by linear regression equations (Table I). Bottled juice stored at 30 °C yielded a linear profile similar to canned juice at 30 °C, whereas the best equation for 40 °C stored bottled juice yielded a curvilinear profile. The equation that described 50 °C stored juice contained higher polynomial functions. It was not surprising that complex equations relating to browning would emerge from these studies in light of recent findings by Rouseff and co-workers (1989) who separated many brown pigments that changed with time and temperature at different rates.

Passy and Mannheim (1979) determined activation energies for browning by plotting the rates of browning versus the reciprocal of absolute temperatures according to the Arrhenius equation. For accurate Arrhenius plots, one must assume that the reaction constant (whether zero or first order) is constant over a defined period of time at a specified temperature. Passy and Mannheim (1979) studied reaction rates for browning over the temperature range 4–35 °C and reported that while the rates for each temperature differed, the reaction constants for each of the temperatures were constant with time.

In our studies with canned and bottled juices stored at 40 and 50 °C, nonuniform browning rates were recorded over the 18-week storage period. Arrhenius plots could not be applied with these nonuniform reaction con-

Table I. Regression Analyses of Canned and Bottled Grapefruit Juice[a]

temp, °C	cans	r^2	glass	r^2
10	not significant	N/A[b]	$Y = 0.133107 + 0.001258X$	0.7150
20	not significant	N/A[b]	$Y = 0.139929 + 0.001405X$	0.6067
30	$Y = 0.101155 + 0.001829X$	0.8482	$Y = 0.134548 + 0.007913X$	0.9741
40	$Y = 0.103397 + 0.006913X + 0.000847X^2$	0.9959	$Y = 0.117373 + 0.034849X - 0.000478X^2$	0.9753
50	$Y = 0.101222 + 0.029452X + 0.000375X^2$	0.9947	$Y = 0.137607 + 0.090707X - 0.004698X^2 + 0.000124X^3$	0.9973

[a] All listed regression equations are significant at $p < 0.05$, where Y = absorbance at 420 nm, X = week. [b] Not applicable.

ties, for example, activation energies.

We believe browning in citrus juices involves a complex group of reactants (Clegg, 1964; Clegg and Morton, 1965; Kanner et al., 1981; Lee and Nagy, 1988a,b) that produce an assortment of brown pigments of highly unstable characteristics (Rouseff et al., 1989). On the basis of recent results of brown pigment formation (Rouseff et al., 1989), we believe it is inaccurate to define browning by a simple zero- or first-order reaction. Simple reaction-order kinetics as used by Passy and Mannheim (1979) and Saguy et al. (1978) assume that the reaction proceeds via a specific pathway yielding specific colored products. Rouseff et al. (1987, 1989) have shown that numerous brown pigments are formed, with some increasing and others decreasing with time. Brown pigment formation indicated the presence of parallel, sequential, and/or competing pathways with multiple reaction kinetics. Thus, it is inappropriate to compute reaction kinetics based on relative changes in the browning intensity of citrus juice solutions. General measurements, such as absorption at 420 nm, would be appropriate only if defined reactants yielded specific, nonchanging pigments. This is clearly not the case for stored citrus juices. Therefore, no simplistic models should be applied to define the complex series of events leading to brown discoloration of citrus juices, especially within the temperature region 30–50 °C.

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