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Kinetics of Nonenzymatic Browning Reaction in Citrus Juice Concentrates during Storage

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Abstract: The kinetics of nonenzymatic browning in citrus juice concentrates (orange, lemon, grapefruit and tangerine) during 8 weeks of storage at 28, 37 and 45 °C were investigated. Browning development was followed by measuring absorbance at 420 nm (A_{420}) and using CIE-Lab color system. Analysis of kinetic data from A_{420} values suggested a zero-order reaction for nonenzymatic browning, while changes in L* and b* parameters followed a first-order reaction. Activation energy for nonenzymatic browning determined by A_{420} values ranged from 17.60 to 35.27 kcal mol^{-1}, while those for L* and b* parameters were 6.67-28.99 kcal mol^{-1} and 15.38-34.2 kcal mol^{-1}, respectively. Activation energies were higher in orange (28.99-35.27 kcal mol^{-1}) and tangerine (27.84-33.1 kcal mol^{-1}) juice concentrates than those in grapefruit (6.74-27.81 kcal mol^{-1}) and lemon (6.67-17.6 kcal mol^{-1}) juice concentrates. The lower activation energies determined for grapefruit and lemon juice concentrates indicated that nonenzymatic browning reactions are favored in these samples.

Key Words: Citrus juice concentrate, nonenzymatic browning, color, storage, kinetic

Turunçgil Suyu Konsantrelerinin Depolanmasında Enzimatik Olmayan Esmerleşme Reaksiyon Kinetiği

Özet: 28, 37 ve 45 °C'de 8 haftalık bir depolama süresince turunçgil suyu konsantrelerinde (portakal, limon, greypfrut ve mandarin) enzimatik olmayan esmerleşme kinetiği incelenmiştir. Esmerleşme, 420 nm'de absorbans ölçülerek ve CIE-Lab renk sistemi kullanılarak izlenmiştir. L* ve b* parametrelerindeki değişim birinci dereceden bir reaksiyon izlemekteyken, A_{420} değerlerine ait kinetik veri analizi sıfırıncı dereceden bir reaksiyonu göstermektedir. A_{420} değerlerinden belirlenen aktivasyon enerjisi 17.6 ile 35.27 kcal mol^{-1} arasında değişmekteyken, L* ve b* parametrelerinden hesaplanan değerler sırasıyla 6.67-28.99 kcal mol^{-1} ve 15.38-34.2 kcal mol^{-1} aralığında değişmektedir. A_{420}, L* ve b* parametrelerinden hesaplanan aktivasyon enerjileri portakal (28.99-35.27 kcal mol^{-1}) ve mandarin (27.84-33.1 kcal mol^{-1}) suyu konsantrelerinde greypfrut (6.74-27.81 kcal mol^{-1}) ve limon (6.67-17.6 kcal mol^{-1}) suyu konsantrelerininkinden daha yüksek bulunmuştur. Greypfrut ve limon suyu konsantreleri için belirlenen daha düşük aktivasyon enerjileri, bu örneklerde enzimatik olmayan esmerleşme reaksiyonlarının teşvik edildiğini göstermektedir.

Anahtar Sözcükler: Turunçgil suyu konsantresi, enzimatik olmayan esmerleşme, renk, depolama, kinetik

Introduction

Browning reactions in foods are widespread phenomena that take place during processing and storage (Eskin, 1990). These reactions involve caramelization, ascorbic acid degradation and the Maillard reaction (Clegg, 1964). Since nonenzymatic browning affects the sensory characteristics of cooked foods such as flavor, aroma and color (Gazzani et al., 1987), it may be desirable in baked, fried or roasted foods (Ashoor and Zent, 1984) as in the manufacture of coffee, tea, beer, bread and cake (Martins et al., 2001). However, nonenzymatic browning reactions are often responsible for important quality changes that occur during the storage of foods, limiting their shelf-life (Buera et al., 1987). For instance, browning is the most common quality problem of many concentrated fruit juices (Toribio and Lozano, 1984) and causes loss of nutrients and the formation of intermediate undesirable compounds, like furfural and 5-hydroxymethylfurfural (Buedo et al., 2001).

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In citrus juices, nonenzymatic browning is due to the reactions of sugars, amino acids and ascorbic acid (Johnson et al., 1995). However, the decomposition of ascorbic acid is reported to be the major deteriorative reaction occuring during the storage of orange juice (Solomon et al., 1995). Lee and Nagy (1988) also reported a high correlation between the percentage loss of ascorbic acid and an increase in browning in grapefruit juices. On the other hand, sugar-amino acid reactions of the classsical Maillard type are of minor importance in citrus juice browning because of the high acidity (pH 2.0-4.0) involved (Clegg, 1964).

However, the presence of amino acids in ascorbate systems is also considered a major contributor to the development of browning (Robertson and Samaniego, 1986). This is illustrated by the fact that the main degradation product of juices with pH values below 4.0 is furfural (Huelin et al., 1971). Furfural is known to undergo polymerization and, as an active aldehyde, may combine with amino acids and contribute to the browning of the juice (Solomon et al., 1995). Likewise, HMF concentration has a high correlation with the level of browning in lemon juice and therefore plays an important role in the formation of brown pigments (Robertson and Samaniego, 1986).

Browning in citrus juices has been studied by a number of investigators (Babsky et al., 1986; Robertson and Samaniego, 1986; Handwerk and Coleman, 1988; Rouseff et al., 1989; Nagy et al., 1990; Nagy et al., 1992; Johnson et al., 1995). The most common method for characterizing browning is the measurement of absorbance at 420 nm (A_{420}).

The main objective of this study was to determine the kinetics of brown color development in citrus juice concentrates by measuring both water soluble brown pigments (A_{420}) and CIE-Lab color indices. Another goal of this study was to determine the correlation between the data obtained from both color measurement systems.

Materials and Methods

Materials

Commercially processed citrus juice concentrates– lemon (44.5 ºBx), orange (61.0 ºBx), grapefruit (59.0 ºBx) and tangerine (59.5 ºBx)– were obtained from a local processing company. The pH values of lemon, orange, grapefruit and tangerine juice concentrates were 1.83, 3.20, 2.57 and 3.23, respectively. All citrus juice concentrates in glass jars were stored in darkness at 28, 37 and 45 ºC for 8 weeks. Browning was measured weekly with 2 replications.

Methods

The soluble solids content of concentrates was determined as ºBx using a refractometer (N.O.W., Nippon Optical Work Co., Ltd., Tokyo). The pH of samples was determined with a pH meter (Consort P407, Schott Gerate, Belgium).

Color measurement: Browning development was determined using 2 color measurement methods: (i) absorbance at 420 nm, (ii) CIE-Lab Color Scale.

i. Determination of water soluble brown pigments: Nonenzymatic browning was monitored using the method of Nagy et al. (1990) on a Unicam UV-VIS (UV2) spectrophotometer in 10 mm cells against water at 420 nm. For this purpose, lemon, orange, grapefruit and tangerine juice concentrates were diluted with distilled water to their ºBx levels of reconstituted juice from concentrates reported in Codex (2001) as 8.0, 11.2, 10.0 and 11.2, respectively.

ii. CIE-Lab Color System: CIE L* (lightness) and b* (yellowness) values were measured with a Minolta CR 300 Colorimeter (Minolta, Osaka, Japan) equipped with a DP-300 data processor.

Statistical analysis: Correlation coefficients between absorbance at 420 nm (A_{420}), L* and b* values were determined by MINITAB (Version 13) statistical software. Evaluations were based on a $P < 0.05$ significance level.

Results and Discussion

Browning development in citrus juice concentrates was determined using 2 color measurement methods: determination of soluble brown pigments as absorbance at 420 nm (A_{420}) and measurement of CIE L*, and b* values.

Absorbance at 420 nm has generally been used by other researchers (Johnson et al., 1995; Kacem et al., 1987) to determine the browning rate in citrus juices. In addition, CIE color indices have also been used for measuring browning in foods (Lee and Nagy, 1988; Ibarz et al., 1999). Zero- and first-order kinetic models were used to evaluate data from A_{420}, L* and b*, which are the best parameters for the determination of browning in citrus juices. The most appropriate model was selected on the basis of determination coefficients (R^2) obtained from regression analysis. Rate constants were determined from best-fit regression equations.

Changes in A_{420}, L* and b* values for citrus juice concentrates during 8 weeks of storage at 28, 37 and 45 °C are shown in Figures 1-3, respectively. Nonenzymatic browning was described as a zero-order reaction since regression analysis of A_{420} values and time gave a linear relationship (Figure 1). The kinetic parameters for A_{420} are given in Table 1.

Previous studies on nonenzymatic browning reactions based on A_{420} measurement in citrus juices (Saguy et al., 1978), apple juices (Lozano, 1991; Burdurlu and Karadeniz, 2002), pear puree (Ibarz et al., 1999), pear juice concentrate (Beveridge and Harrison, 1984), and

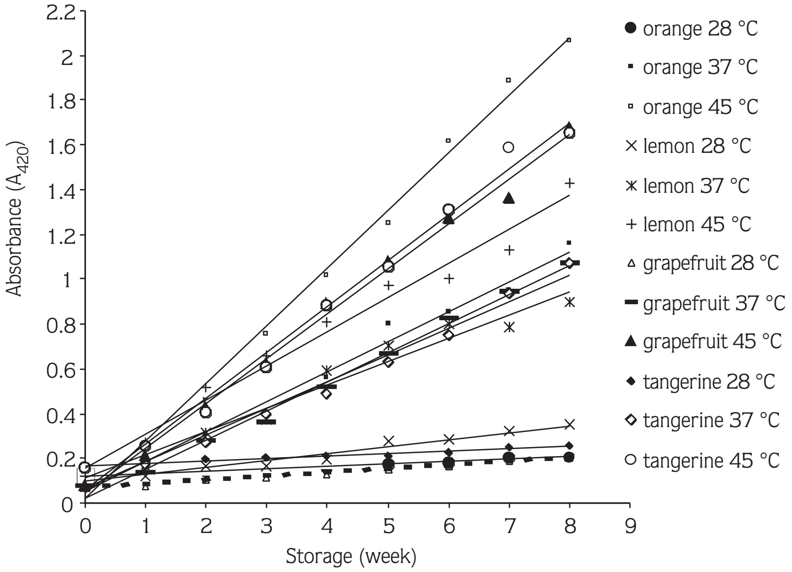

Figure 1. Changes in absorbance at 420 nm for citrus juice concentrates during storage.

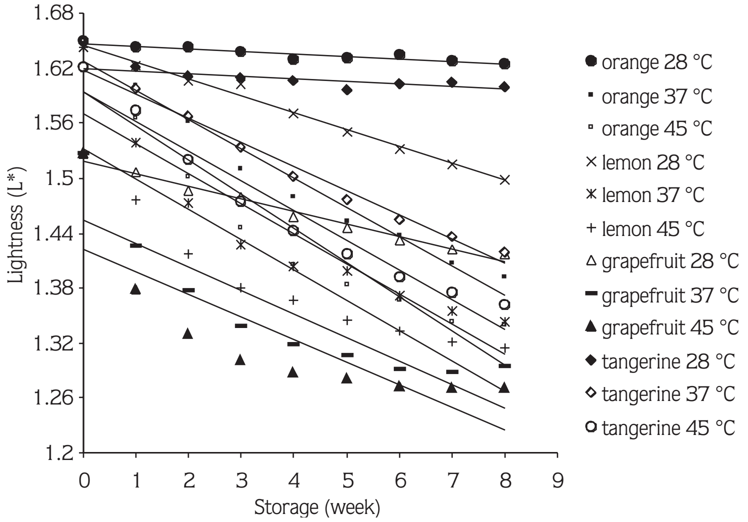

Figure 2. Changes in lightness value (L*) of citrus juice concentrates during storage.

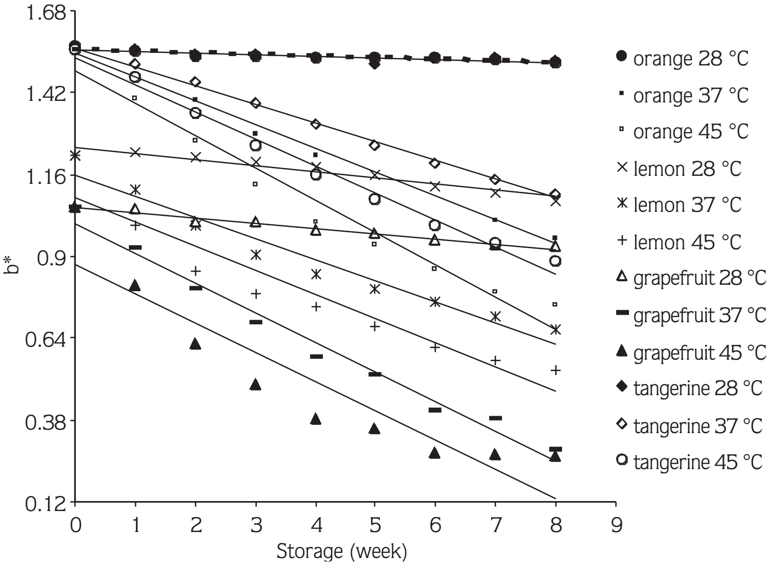

Figure 3. Changes in b* for citrus juice concentrates during storage.

Table 1. Kinetic parameters for water soluble brown pigments (A_{420}) in citrus juice concentrates[a].

				Q_{10}		
Species	Temperature (℃)	-lnk	Ea (kcal mol^{-1})	28-37 ℃	28-45 ℃	37-45 ℃
	28	4.5008 (0.9803)	35.27 (0.9328)	15.88	6.35	2.26
Orange	37	2.0122 (0.9832)				
	45	1.3591 (0.9934)				
	28	3.4609 (0.9573)	17.60 (0.9471)	3.80	2.53	1.59
Lemon	37	2.2586 (0.9664)				
	45	1.8859 (0.9803)				
	28	4.0804 (0.9878)	27.81 (0.9150)	9.68	4.28	1.71
Grapefruit	37	2.0372 (0.9933)				
	45	1.6084 (0.9942)				
	28	4.4741 (0.9675)	32.39 (0.9224)	13.5	5.46	2.46
Tangerine	37	2.1312 (0.9784)				
	45	1.5877 (0.9883)				

[a] Numbers in brackets represent the determination coefficients (R^2)

intermediate moisture apples (Singh et al., 1983) also confirmed that the reactions followed zero-order kinetics. On the other hand, a first-order browning reaction was reported in orange juice serum (Johnson et al., 1995) and apple juice concentrates (Toribio and Lozano, 1984). In addition, a parabolic kinetic model of the nonenzymatic browning reaction of peach juice concentrate was determined by Buedo et al. (2001) on the basis of A_{420}.

The kinetics of the change in L* and b* values in citrus juice concentrates were also evaluated. L* and b* values decreased as a function of storage time and temperature (Figures 2 and 3), indicating that the color of samples changed from yellow to brown. Since regression analysis of the logarithm of L* and b* values and time gave a higher linear relationship, first-order kinetics were used to evaluate these color data. The first-order kinetic model was also applied to L* changes by Lozano and Ibarz

(1997) for thermally treated apple, peach and prune purees, and by Ibarz et al. (1999) for pear puree. Thermal degradation of the color in peach puree using L* and b* parameters was also found to be a first-order reaction by Ávila and Silva (1999).

The temperature dependence of browning was determined by calculating activation energies (E_a) and temperature quotients (Q_{10}) by Eqs. 1 and 2, and Arrhenius plots for A_{420} values are given in Figure 4. As shown in Table 1, the E_a values for A_{420} results ranged from 17.60 to 35.27 kcal mol^{-1} and Q_{10} values from 1.59 to 15.88. The E_a values were comparable with those reported by Johnson et al. (1995) in orange juice serum (19-25 kcal mol^{-1}) and by Ibarz et al. (1999) in the liquid fraction of pear puree (15 kcal mol^{-1}). Furthermore, these values are in the range normally expected for nonenzymatic browning reactions (16.7-43.0 kcal mol^{-1}) (O'Brien, 1996).

Activation energies for L* and b* parameters were calculated from the slopes of the Arrhenius plots shown in Figures 5 and 6. Tables 2 and 3 shows the activation energies (E_a) and Q_{10} values for L* and b* parameters. While the E_a values for the L* parameter of citrus juice concentrates ranged from 6.67 to 28.99 kcal mol^{-1}, those for the b* parameters ranged from 15.38 to 34.2 kcal mol^{-1}. In relation to parameter L*, an activation energy value of 18.3 kcal mol^{-1} was obtained for the liquid fraction of pear puree by Ibarz et al. (1999).

$$k = ko.\ e^{-Ea/RT} \quad \text{..} \quad (1)$$

k = rate constant ($week^{-1}$)

ko = pre-exponential factor ($week^{-1}$)

E_a = activation energy (kcal mol^{-1})

R = gas constant (1.987 cal^{-1} mol ^{O}K)

T = absolute temperature (ºK)

$$Q_{10} = [k_2/k_1]^{10/T2-T1} \quad \text{..} \quad (2)$$

k_1 = rate constant at T_1

k_2 = rate constant at T_2

T_1, T_2 = absolute temperature (°K)

Q_{10} values obtained from A_{420}, L* and b* parameters were higher in orange (pH 3.20) and tangerine (pH 3.23) juice concentrates than those in grapefruit (pH 2.56) and lemon (pH 1.82) juice concentrates. This result indicated

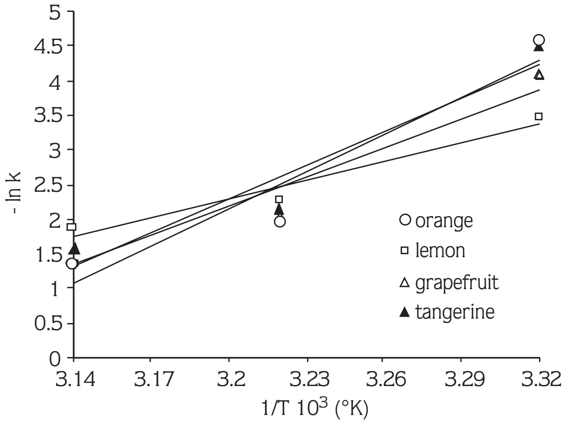

Figure 4. Arrhenius plots for A_{420} values in citrus juice concentrates.

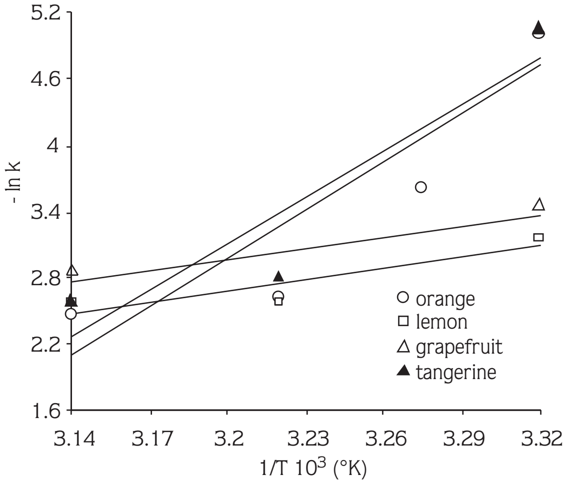

Figure 5. Arrhenius plots of L* in citrus juice concentrates.

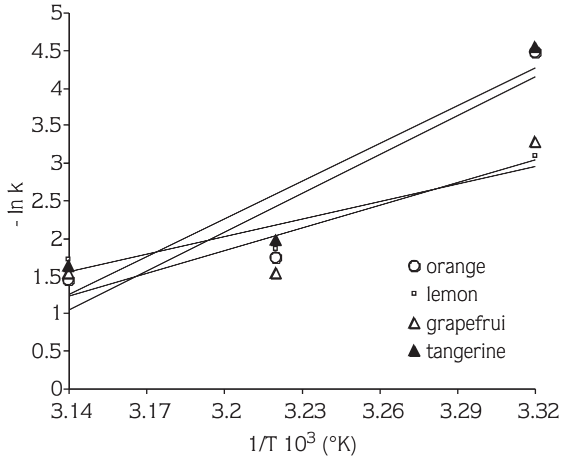

Figure 6. Arrhenius plots of b* in citrus juice concentrates.

Table 2. Kinetic parameters for lightness value (L*) in citrus juice concentrates[a].

Species	Temperature (℃)	-lnk	Ea (kcal mo^{-1})	Q_{10}		
				28-37 ℃	28-45 ℃	37-45 ℃
Orange	28	5.0056 (0.8642)	28.99 (0.8447)	14.35	4.49	1.21
	37	2.6078 (0.9681)				
	45	2.4522 (0.9017)				
Lemon	28	3.1653 (0.9909)	6.67 (0.7997)	1.92	1.41	0.99
	37	2.5770 (0.8544)				
	45	2.5801 (0.7434)				
Grapefruit	28	3.4546 (0.9802)	6.74 (0.7574)	2.01	1.41	0.95
	37	2.8271 (0.7780)				
	45	2.8667 (0.6539)				
Tangerine	28	5.0515 (0.7328)	27.84 (0.8621)	12.1	6.87	1.86
	37	2.8078 (0.9896)				
	45	2.5929 (0.9551)				

[a] Numbers in brackets represent the determination coefficients (R^2)

Table 3. Kinetic parameters for b* values in citrus juice concentrates[a].

Species	Temperature (℃)	-lnk	Ea (kcal mol^{-1})	Q_{10}		
				28-37 ℃	28-45 ℃	37-45 ℃
Orange	28	4.4641 (0.7806)	34.20 (0.8711)	20.44	5.91	1.47
	37	1.7494 (0.9915)				
	45	1.4427 (0.9657)				
Lemon	28	3.0879 (0.9450)	15.38 (0.8689)	3.90	2.22	1.18
	37	1.8629 (0.9596)				
	45	1.7297 (0.9059)				
Grapefruit	28	3.2702 (0.9706)	19.77 (0.7995)	6.94	2.77	0.99
	37	1.5271 (0.9806)				
	45	1.5367 (0.8551)				
Tangerine	28	4.5475 (0.6754)	33.10 (0.8852)	17.3	5.60	1.57
	37	1.9809 (0.9976)				
	45	1.6180 (0.9890)				

[a] Numbers in brackets represent the determination coefficients (R^2)

that nonenzymatic browning reactions in orange and tangerine juice concentrates are more sensitive to temperature rises. On the basis of browning rates, E_a values followed the same trend as Q_{10} values for all citrus juice concentrates. Thus, it is suggested that browning in orange and tangerine juice concentrates is more temperature dependent. On the other hand, the development of browning in lemon and grapefruit juice concentrates may be attributed to their higher acidity. Since ascorbic acid, having a central role in the browning of citrus juices and concentrates (Eskin, 1990), decomposes easily in strongly acid solution (Huelin et al., 1971), the development of color in these concentrates is rapidly accelerated.

The best-fit model for L* and b* parameters was first order, while a zero-order kinetic model was best described for A_{420} in citrus juice concentrates. Even though there were differences between the reaction kinetic models in relation to the parameters L*, b* and A_{420}, significant correlations ($P < 0.05$) were found among these parameters in all citrus juice concentrates at all temperatures studied. These differences in describing the nonenzymatic browning order may be due to A_{420} values demonstrating soluble brown pigments while L* and b* parameters indicate visual evaluation of citrus juice concentrates. In addition, as pointed out by Labuza and Riboh (1982), the statistical difference between zero- and first-order reactions may also be insignificant.

Conclusion

In this study, a zero-order browning reaction was determined depending on A_{420} values, while a first-order kinetic model was best described by L* and b* parameters. The difference in the nonenzymatic browning order may be due to A_{420} values demonstrating soluble brown pigments, whereas L* and b* parameters indicate a visual evaluation of citrus juice concentrates. Nonenzymatic browning occurred easily in lemon and grapefruit juice concentrates because of their relatively lower E_a values. Significant correlations were obtained between A_{420} and CIE-Lab color parameters (L*, b*), suggesting that all 3 values would be suitable as indices of browning.

Since quality is supremely important in food, deterioration has to be controlled during storage. In concentrated juices, one of the main causes of deterioration is nonenzymatic browning, since enzymatic browning is eliminated by heat treatment during processing. Therefore, kinetic modelling of nonenzymatic browning reactions is very important for fruit juice storage. From a practical standpoint, by measuring the rate and temperature-dependence of nonenzymatic browning reactions, it is possible to determine the period of storage at a given temperature without any quality deterioration.

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