

Degradation of vitamin C in citrus juice concentrates during storage

Hande Selen Burdurlu, Nuray Koca, Feryal Karadeniz *

Ankara University, Faculty of Engineering, Food Engineering Department, Campus of Agricultural Faculty, Diskapı 06110 Ankara, Turkey

Received 16 July 2004; accepted 7 March 2005

Available online 11 May 2005

Abstract

Kinetics of ascorbic acid degradation in citrus juice concentrates (orange, lemon, grapefruit, tangerine) during an eight week storage at 28, 37 and 45 °C were investigated. The loss of ascorbic acid at each temperature followed a first-order kinetic model. Activation energy was determined in the range of 12.77 ± 0.97 – 25.39 ± 1.98 kcal mol⁻¹. Ascorbic acid retention after storage at 28, 37 and 45 °C was about 54.5–83.7%, 23.6–27% and 15.1–20.0%, respectively. Since hydroxymethylfurfural (HMF) is one of the decomposition compounds of ascorbic acid degradation, its formation was also investigated. HMF accumulation fitted to a zero-order kinetic model and activation energy ranged from 43.41 ± 0.67 to 80.02 ± 0.07 kcal mol⁻¹. Significant correlation was obtained between HMF accumulation and ascorbic acid loss at all storage temperatures in all citrus juice concentrates.

© 2005 Elsevier Ltd. All rights reserved.

Keywords: Citrus juice concentrates; Ascorbic acid; HMF; Kinetics; Storage

1. Introduction

Nutritional quality of food during storage has become increasingly important problem. The loss of some nutrients such as ascorbic acid (vitamin C) might be a critical factor for the shelf life of some products as citrus juice concentrates (Laing, Schlueter, & Labuza, 1978) since vitamin C content of citrus juices undergoes destruction during storage (Johnson, Braddock, & Chen, 1995; Lee & Nagy, 1988a; Solomon, Svanberg, & Sahlström, 1995).

Ascorbic acid (AA) is an important component of our nutrition and used as additive in many foods because of its antioxidant capacity. Thus, it increases quality and technological properties of food as well as nutritional value (Larisch, Groß, & Pischetsrieder, 1998; Solomon et al., 1995). However, AA is an unstable compound and under less desirable conditions it decomposes easily (Fennema, 1977; Lee & Coates, 1999).

Degradation of AA proceeds both aerobic and anaerobic pathways (Huelin, 1953; Johnson et al., 1995) and depends upon many factors such as oxygen, heat, light (Robertson & Samaniego, 1986), storage temperature and storage time (Fellers, 1988; Gordon & Samaniego-Esguerra, 1990). Oxidation of ascorbic acid occurs mainly during the processing of citrus juices (Huelin, 1953), whereas, anaerobic degradation of AA mainly appears during storage (Johnson et al., 1995; Lee & Nagy, 1988a; Solomon et al., 1995) which is especially observed in thermally preserved citrus juices. It was reported that several decomposition reactive products occur via the degradation of vitamin C (Eskin, 1990; Huelin, Coggiola, Sidhu, & Kennett, 1971) and these compounds may combine with amino acids, thus result in formation of brown pigments (Clegg, 1964; Larisch et al., 1998). Hydroxymethylfurfural (HMF) is one of the decomposition products of ascorbic acid (Eskin, 1990; Solomon et al., 1995) and suggested that a precursor of brown pigments. It is used to evaluate severity of heating applied to fruit juices during processing and taken into account for quality control (Lee & Nagy, 1988b). Other pathways of HMF accumulation are

* Corresponding author. Tel.: +90 312 3170550x1716; fax: +90 312 3178711.

E-mail address: karadeni@eng.ankara.edu.tr (F. Karadeniz).

known as degradation of reducing sugars (Ibarz, Pagán, & Garza, 1999; Lee & Nagy, 1988b) and Maillard reaction (Yaylayan, 1990).

Since ascorbic acid degradation cause browning which is the other problem of quality loss in citrus juices during storage (Nagy, Rouseff, Fisher, & Lee, 1992; Tatum, Philip, & Berry, 1969), it is necessary to describe ascorbic acid degradation and investigate kinetics of AA loss in stored citrus juices.

The objective of this study was to determine kinetics of both ascorbic acid degradation and HMF formation in citrus juice concentrates during storage.

2. Materials and methods

2.1. Materials

Orange, lemon, grapefruit and tangerine juice concentrates at 61°, 44.5°, 59° and 59.5° Bx, respectively, were obtained from one of fruit juice producers in Turkey. All citrus juice concentrates in glass jars were stored in darkness at 28, 37 and 45 °C for eight weeks. Ascorbic acid and HMF contents were determined every week and analyses were carried out on two replicates.

2.2. Methods

2.2.1. Determination of soluble solids content and pH value

The soluble solids content of concentrates was determined as ° Bx using a refractometer (NOW, Nippon Optical Work Co., LTD., Tokyo). The pH of samples was determined with a pH meter (Consort P407, Schott Gerate, Belgium).

2.2.2. Determination of ascorbic acid

The spectrophotometric method (Pepkowitz, 1943; Robinson & Stotz, 1945) for determination of ascorbic acid was performed by using Unicam UV–VIS (UV-2) spectrophotometer at a wavelength of 500 nm against xylene. The loss of ascorbic acid in citrus juice concentrates was calculated by using the standard equation for a first-order reaction given below:

$$\ln C = \ln C_0 - kt$$

where C , the concentration at time t ; C_0 , the concentration at time zero; k , the first-order rate constant; t , the storage time (week).

2.2.3. Determination of HMF

Colorimetric method was used for determination of HMF. This method is based on measurement of red color appears from reaction between thiobarbituric acid (TBA) and HMF on spectrophotometer at 550 nm against water (Koch, 1966).

2.2.4. Statistical analysis

Correlation coefficients between ascorbic acid degradation and HMF were performed by MINITAB (Version of Release,13) statistical computer programme.

3. Results and discussion

Initial vitamin C contents of orange, lemon, grapefruit and tangerine juice concentrates were 232.9, 225, 205.8 and 97.9 mg/100 g, respectively (Table 1). After an eight week storage, ascorbic acid contents of those samples at 28, 37 and 45 °C decreased to 194.9, 122.8, 144.0, 65 mg/100 g; 52.4, 54.6, 55.5, 23.1 mg/100 g and 39.3, 45, 31.4, 14.8 mg/100 g, respectively. It was observed that ascorbic acid decreased with increasing temperature as expected and retention of vitamin C (%) in those samples at 28, 37 and 45 °C was 83.7, 54.5, 70, 66.4; 22.5, 24.3, 27, 23.6 and 16.9, 20, 15.3, 15.1, respectively. At storage temperature of 28 °C, the loss of vitamin C in orange juice concentrate was lowest compared to the loss of other concentrates. Moreover, half destruction time of vitamin C was found higher in orange juice concentrate among the other samples (Table 2). Ascorbic acid retentions in all concentrates at 37 and 45 °C were found almost similar.

When ascorbic acid retention of citrus juice concentrates plotted to versus storage time, determination coefficients of the curves found between 0.8635 and 0.9702. However, the plot of change in logarithm of ascorbic acid retentions yielded higher determination coefficients (Table 2). So, the loss of ascorbic acid in citrus juice concentrates at all temperatures was described as a first-order reaction. A representative graph for log percent retention of ascorbic acid in grapefruit juice concentrates is shown in Fig. 1.

The first order kinetic model for ascorbic acid degradation determined in this study is in agreement with the other studies (Huelin, 1953; Johnson et al., 1995; Johnson & Toledo, 1975; Lathrop & Leung, 1980; Lee & Coates, 1999). On the other hand, there have been studies reported that ascorbic acid destruction follows a zero-order (Laing et al., 1978) or second-order reaction (Robertson & Samaniego, 1986). Lee and Coates (1999) is also reported that the loss of vitamin C known to follow first order reaction for orange juice stored below 50 °C.

Temperature dependence of ascorbic acid degradation was determined by using the Arrhenius equation:

$$k = k_0 \cdot e^{-E_a/RT}$$

k = rate constant; k_0 = pre-exponential factor; E_a = activation energy (kcal mol⁻¹); R = gas constant (1.987 kcal mol⁻¹ K⁻¹); T = absolute temperature in K.

Table 1
Vitamin C degradation in citrus juice concentrates during storage (mg/100 g)

Variety	Temperature (°C)	Storage (week)								
		0	1	2	3	4	5	6	7	8
Orange	28	232.9	242.1	226.4	218.5	214.0	210.0	207.0	189.9	194.9
	37	232.9	208.0	196.6	138.9	121.5	106.2	91.3	69.0	52.4
	45	232.9	198.8	153.4	95.2	72.9	56.3	39.3	38.4	39.3
Lemon	28	225.0	198.8	188.8	173.5	166.9	163.8	148.1	139.8	122.8
	37	225.0	188.3	153.4	118.8	80.4	73.4	101.8	49.8	54.6
	45	225.0	191.4	152.9	109.2	112.7	80.4	65.9	50.6	45.0
Grapefruit	28	205.8	194.0	184.4	164.3	160.0	159.1	155.0	139.9	144.0
	37	205.8	180.0	136.8	119.9	108.3	95.7	82.1	60.7	55.5
	45	205.8	152.0	115.8	90.9	71.2	44.1	41.9	36.7	31.4
Tangerine	28	97.9	95.3	80.4	80.9	81.5	73.0	77.0	70.0	65.0
	37	97.9	88.7	68.6	60.3	55.0	34.1	38.5	38.4	23.1
	45	97.9	68.6	51.5	40.6	30.1	24.0	18.7	13.9	14.8

Table 2
Times of half destruction of ascorbic acid and determination coefficients for ascorbic acid degradation and HMF accumulation in citrus juice concentrates

Species	Temperature °C	Times of half destruction and determination coefficients of first-order ascorbic acid degradation			Determination coefficients of zero-order HMF formation	
		$t_{1/2}$ (week)	$k \pm \text{SD}$	R^2	$k \pm \text{SD}$	R^2
Orange	28	24.75	0.0276 ± 0.0108	0.9107	0.2698 ± 0.0340	0.9194
	37	3.75	0.1850 ± 0.0133	0.9793	80.728 ± 25.0024	0.9225
	45	2.72	0.2550 ± 0.0287	0.9512	333.40 ± 34.9729	0.9207
Lemon	28	10.34	0.0670 ± 0.0059	0.9742	3.788 ± 0.6734	0.9518
	37	3.79	0.1830 ± 0.0041	0.8849	76.057 ± 27.9078	0.9451
	45	3.35	0.2070 ± 0.0330	0.9869	181.940 ± 21.3965	0.9848
Grapefruit	28	14.74	0.0470 ± 0.0067	0.9326	3.7012 ± 0.5946	0.9359
	37	4.25	0.1626 ± 0.0197	0.9862	151.35 ± 38.5209	0.9724
	45	2.86	0.2420 ± 0.0184	0.9740	438.75 ± 41.1638	0.9744
Tangerine	28	15.06	0.0460 ± 0.0033	0.8877	0.3965 ± 0.0177	0.9522
	37	4.15	0.1670 ± 0.0108	0.9274	64.368 ± 12.8144	0.9618
	45	2.79	0.2480 ± 0.0297	0.9790	315.77 ± 34.1946	0.9523

SD: Standard deviation.

Activation energies (Table 3) were calculated by using Arrhenius plots of ascorbic acid degradation in citrus juice concentrates given in Fig. 2 and found higher in orange (pH 3.20), tangerine (pH 3.23) and grapefruit (pH 2.56) juice concentrates than that of lemon (pH 1.82) juice concentrates (Table 3). Activation energies (E_a) calculated for ascorbic acid degradation in citrus juice concentrates were related with those reported by Johnson et al. (1995) (30 kcal mol^{-1} in orange juice serum) and Laing et al. (1978) ($14\text{--}17 \text{ kcal mol}^{-1}$ in an intermediate moisture model system).

Temperature quotient (Q_{10}) values were also calculated for the temperature ranges of 28–37 °C, 28–45 °C and 37–45 °C (Table 3). According to these values, the least effect of temperature rise on ascorbic acid degradation was observed in lemon juice concentrate. However, it can be easily seen that the reaction occurred in orange

juice concentrate was highly affected by temperature increase except at the range of 37–45 °C.

HMF concentration of citrus juice concentrates is given in Table 4. As can be seen in Table 4, after an eight week storage, HMF contents of citrus juice concentrates at 28 °C were ranged from 3.01 to 28.32 mg/kg. The variation of HMF values at 37 °C was between 521.52 and 1141.99 mg/kg, while those values for 45 °C ranged from 1401.1 to 3252.3 mg/kg. The increase of HMF at 45 °C was approximately 2.7 times higher than that of at 37 °C. When HMF values of citrus juice concentrates plotted to versus storage time the best fit model for HMF accumulation was zero-order and the determination coefficients in relation to this reaction were shown in Table 2. A representative graph for HMF formation in citrus juice concentrates is given in Fig. 3.

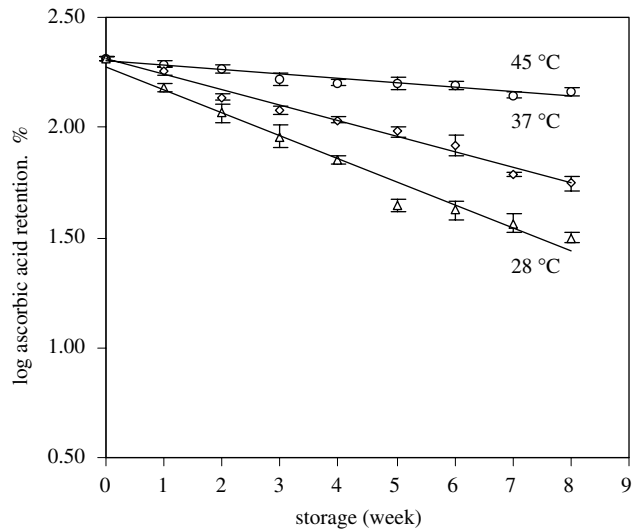


Fig. 1. Ascorbic acid loss in grapefruit juice concentrates during storage.

Significant correlation (0.780–0.967) was obtained between ascorbic acid loss and HMF formation ($p < 0.05$) during storage of citrus juice concentrates. HMF formation in citrus juice concentrates is mainly attributed to decomposition of ascorbic acid. In addition, sugar degradation might also be attributed to HMF content, since it is known that this reaction occurs in acidic media (Ibarz et al., 1999; Lee & Nagy, 1988b). However Maillard reaction, known as the other pathway for HMF accumulation, is thought to have a minor effect on HMF accumulation since Maillard reaction was retarded by acidic systems (Daniel & Whistler, 1985).

Fig. 4 shows Arrhenius plots of HMF accumulation in citrus juice concentrates. Activation energies and Q_{10} values of HMF formation were calculated in citrus juice concentrates and given in Table 3. In citrus juice concentrates activation energies for HMF formation were obtained as in the range of 43.41 ± 0.67 – 80.02 ± 0.07 kcal mol⁻¹. High activation energies and Q_{10} values in orange and tangerine juice concentrates

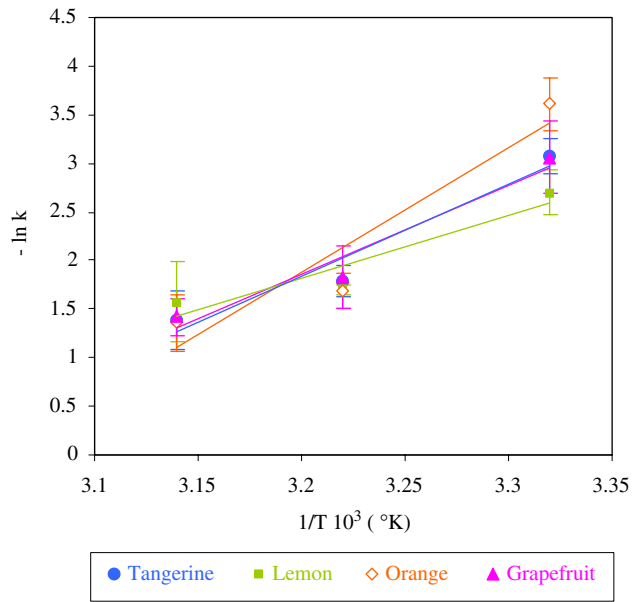


Fig. 2. Arrhenius plots of ascorbic acid degradation in citrus juice concentrates.

indicated that HMF formation was more temperature dependent than the other samples. The lowest E_a value for HMF formation was obtained in lemon juice concentrate. The lowest activation energies determined in lemon juice concentrates for ascorbic acid degradation and HMF accumulation is also remarkable since both reactions are favoured at low pH values even if at low temperatures.

Kinetics of HMF formation was also investigated by other studies and reported that this reaction fitted to a zero-order (Resnik & Chirife, 1979), first-order (Ibarz et al., 1999; Robertson & Samaniego, 1986; Tosi, Ciappini, Ré, & Lucero, 2002) and second-order (Shallenberger & Mattick, 1983) kinetic models. Activation energy for HMF accumulation in apple juice model solution was reported as 28–39.6 kcal mol⁻¹ by Resnik and Chirife (1979) and in pear puree determined as 27.5 kcal mol⁻¹ by Tosi et al. (2002).

Table 3
Activation energies (E_a) and temperature quotient (Q_{10}) values for ascorbic acid degradation and HMF accumulation

Reaction	Species	$E_a \pm \text{SD}$ (kcal mol ⁻¹)	Q_{10}		
			28–37 °C	28–45 °C	37–45 °C
Ascorbic acid degradation	Orange	25.16 \pm 4.29	8.14	3.68	1.50
	Lemon	12.77 \pm 0.97	3.05	1.95	1.17
	Grapefruit	18.37 \pm 1.08	3.98	2.63	1.63
	Tangerine	18.94 \pm 0.74	4.18	2.70	1.65
HMF accumulation	Orange	80.02 \pm 0.07	560.19	66.71	5.89
	Lemon	43.41 \pm 0.67	27.93	9.82	2.97
	Grapefruit	53.52 \pm 1.01	61.50	16.73	3.77
	Tangerine	74.76 \pm 1.15	317.00	51.48	6.46

SD: Standard deviation.

Table 4
HMF formation in citrus juice concentrates during storage (mg/kg)

Variety	Temperature (°C)	Storage (week)								
		0	1	2	3	4	5	6	7	8
Orange	28	1.13	1.13	1.13	1.51	1.88	2.63	2.64	2.64	3.01
	37	1.13	10.57	30.58	90.25	141.99	270.39	358.38	493.58	640.86
	45	1.13	38.51	152.19	352.71	655.96	1138.20	1449.00	1945.60	2727.00
Lemon	28	0.37	5.28	8.68	12.83	19.25	25.30	24.50	29.07	28.32
	37	0.37	42.67	86.10	157.47	233.76	460.35	423.33	526.05	534.36
	45	0.37	112.91	231.87	393.50	538.14	889.72	1024.90	1190.00	1401.10
Grapefruit	28	2.64	4.90	8.30	12.46	16.99	26.05	26.05	28.32	28.32
	37	2.64	45.31	134.44	229.98	421.45	608.00	783.61	994.33	1141.99
	45	2.64	131.04	336.85	745.84	1158.60	1864.80	2355.70	2854.20	3252.30
Tangerine	28	0.37	0.37	1.13	1.51	2.26	2.64	2.79	2.79	3.39
	37	0.37	10.95	39.27	101.58	164.27	294.93	357.25	460.34	521.52
	45	0.37	36.25	161.25	396.52	681.26	1131.00	1604.20	2014.40	2348.20

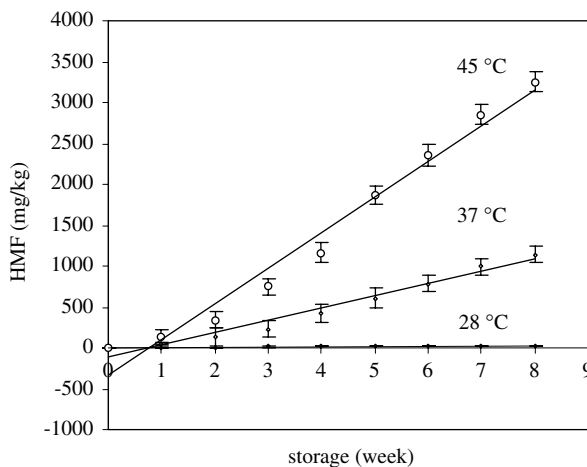


Fig. 3. HMF accumulation in grapefruit juice concentrates during storage.

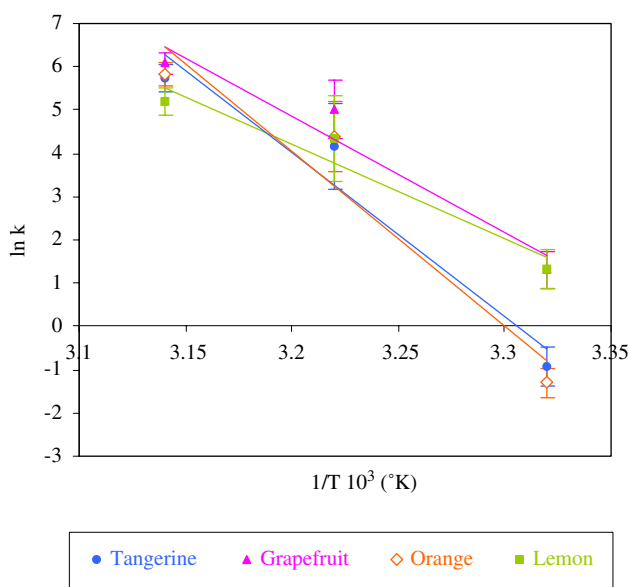


Fig. 4. Arrhenius plots of HMF accumulation in citrus juice concentrates.

4. Conclusion

Ascorbic acid in citrus juice concentrates decreased with increasing temperature. The loss of ascorbic acid in citrus juice concentrates at all storage temperatures was described as a first-order reaction. Orange juice concentrate had the lowest reaction rate at 28 °C when compared to other samples. Since ascorbic acid decomposes easily in acid solutions, lemon juice concentrates (pH 1.82) showed the highest ascorbic acid destruction. On the other hand, HMF accumulation of citrus juice concentrates increased depending on storage temperature. It was observed that the increase of HMF in citrus juice concentrates at 45 °C was approximately 2.7 times higher than that of at 37 °C. High activation energies and Q_{10} values of HMF formation in orange and tangerine juice concentrates indicated that this reaction was more temperature dependent than the other concentrates. The lowest activation energy determined in lemon juice concentrates for HMF accumulation is remarkable since the formation of HMF is favoured at low pH values even if at low temperatures.

References

- Clegg, K. M. (1964). Non-enzymic browning of lemon juice. *Journal of the Science of Food and Agricultural*, 15, 878–885.
- Daniel, J. R., & Whistler, R. L. (1985). Carbohydrates. In O. R. Fennema (Ed.), *Food chemistry* (second ed., pp. 70–137). New York: Marcel Dekker.
- Eskin, N. A. M. (1990). Biochemistry of food processing: Browning reactions in foods. In *Biochemistry of foods* (second ed., pp. 240–295). London: Academic Press.
- Fellers, P. J. (1988). Shelf life and quality of freshly squeezed, unpasteurized, polyethylene-bottled citrus juice. *Journal of Food Science*, 53(6), 1699–1702.
- Fennema, O. (1977). Loss of vitamins in fresh and frozen foods. *Food Technology*, 31(12), 32–38.
- Gordon, L. R., & Samaniego-Esguerra, M. C. (1990). Effect of soluble solids and temperature on ascorbic acid degradation in lemon juice stored in glass bottles. *Journal of Food Quality*, 13, 361–374.

- Huelin, F. E. (1953). Studies on the anaerobic decomposition of ascorbic acid. *Food Research*, 18, 633–639.
- Huelin, F. E., Coggiola, I. M., Sidhu, G. S., & Kennett, B. H. (1971). The anaerobic decomposition of ascorbic acid in the pH range of foods and in more acid solutions. *Journal of the Science of Food and Agricultural*, 22, 540–542.
- Ibarz, A., Pagán, J., & Garza, S. (1999). Kinetic models for colour changes in pear puree during heating at relatively high temperatures. *Journal of Food Engineering*, 39, 415–422.
- Johnson, J. R., Braddock, R. J., & Chen, C. S. (1995). Kinetics of ascorbic acid loss and nonenzymatic browning in orange juice serum: Experimental rate constants. *Journal of Food Science*, 60(3), 502–505.
- Johnson, R. L., & Toledo, R. T. (1975). A research note: Storage stability of 55° Brix orange juice concentrate aseptically packaged in plastic and glass containers. *Journal of Food Science*, 40, 433–434.
- Koch, J. (1966). Die Beurteilung von Fruchtsäften im Hinblick auf ihren HMF Gehalt. *Deutsche Lebensmittel Rundschau*, 62, 105–108.
- Laing, B. M., Schlueter, D. L., & Labuza, T. P. (1978). Degradation kinetics of ascorbic acid at high temperature and water activity. *Journal of Food Science*, 43(5), 1440–1443.
- Larisch, B., Groß, U., & Pischetsrieder, M. (1998). On the reaction of L-ascorbic acid with propylamine under various conditions: quantification of the main products by HPLC/DAD. *Zeitschrift für Lebensmittel-Untersuchung Und-Forschung A*, 206, 333–337.
- Lathrop, P. J., & Leung, H. K. (1980). Rates of ascorbic acid degradation during thermal processing of canned peas. *Journal of Food Science*, 45, 152–153.
- Lee, H. S., & Coates, G. A. (1999). Vitamin C in frozen, fresh squeezed, unpasteurized, polyethylene-bottled orange juice: A storage study. *Food Chemistry*, 65, 165–168.
- Lee, H. S., & Nagy, S. (1988a). Quality changes and nonenzymatic browning intermediates in grapefruit juice during storage. *Journal of Food Science*, 53(1), 168–171.
- Lee, H. S., & Nagy, S. (1988b). Relationship of sugar degradation to detrimental changes in citrus juice quality. *Food Technology*, 11, 91–97.
- Nagy, S., Rouseff, R. L., Fisher, J. F., & Lee, H. S. (1992). HPLC separation and spectral characterization of browning pigments from white grapefruit juice stored in glass and cans. *Journal of Agricultural and Food Chemistry*, 40, 27–31.
- Pepkowitz, L. P. (1943). The rapid determination of ascorbic acid by the adaptation of Stotz's method to plant materials. *Journal of Biological Chemistry*, 151, 405.
- Resnik, S., & Chirife, J. (1979). Effect of moisture content and temperature on some aspects of nonenzymatic browning in dehydrated apple. *Journal of Food Science*, 44(2), 601–605.
- Robertson, G. L., & Samaniego, C. M. L. (1986). Effect of initial dissolved oxygen levels on the degradation of ascorbic acid and the browning of lemon juice during storage. *Journal of Food Science*, 51(1), 184–187.
- Robinson, W. B., & Stotz, E. (1945). The indophenol-xylene extraction method for ascorbic acid and modifications for interfering substances. *Journal of Biological Chemistry*, 160, 217.
- Shallenberger, R. S., & Mattick, L. R. (1983). Relative stability of glucose and fructose at different acid pH. *Food Chemistry*, 12, 159–165.
- Solomon, O., Svanberg, U., & Sahlström, A. (1995). Effect of oxygen and fluorescent light on the quality of orange juice during storage at 8 °C. *Food Chemistry*, 53, 363–368.
- Tatum, J. H., Philip, E. S., & Berry, R. E. (1969). Degradation products from ascorbic acid. *Journal of Agricultural and Food Chemistry*, 17(1), 38–40.
- Tosi, E., Ciappini, M., Ré, E., & Lucero, H. (2002). Honey thermal treatment effects on hydroxymethylfurfural content. *Food Chemistry*, 77, 71–74.
- Yaylayan, V. (1990). In search of alternative mechanisms for the Maillard reaction. *Trends in Food Science and Technology*, 1(7), 20–22.