



# Degradation of vitamin C in citrus juice concentrates during storage

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## 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  $12.77 \pm 0.97$ – $25.39 \pm 1.98$  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  $43.41 \pm 0.67$  to  $80.02 \pm 0.07$  kcal mol $^{-1}$ . Significant correlation was obtained between HMF accumulation and ascorbic acid loss at all storage temperatures in all citrus juice concentrates.

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**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).

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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

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<sup>-1</sup>);  $R$  = gas constant (1.987 kcal mol<sup>-1</sup> K<sup>-1</sup>);  $T$  = 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 <sub>1/2</sub> (week)	k ± SD	R <sup>2</sup>	k ± SD	R <sup>2</sup>
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<sup>-1</sup> in orange juice serum) and Laing et al. (1978) (14–17 kcal mol<sup>-1</sup> 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.

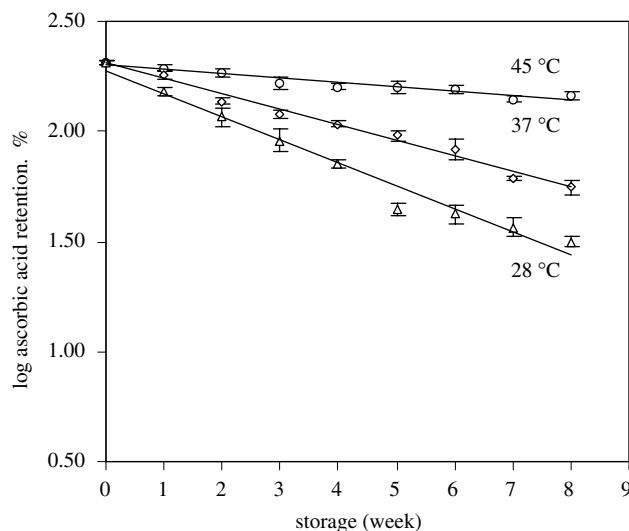


Fig. 1. Ascorbic acid loss in grapefruit juice concentrates during storage.

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  $43.41 \pm 0.67$ – $80.02 \pm 0.07$  kcal mol $^{-1}$ . High activation energies and  $Q_{10}$  values in orange and tangerine juice concentrates

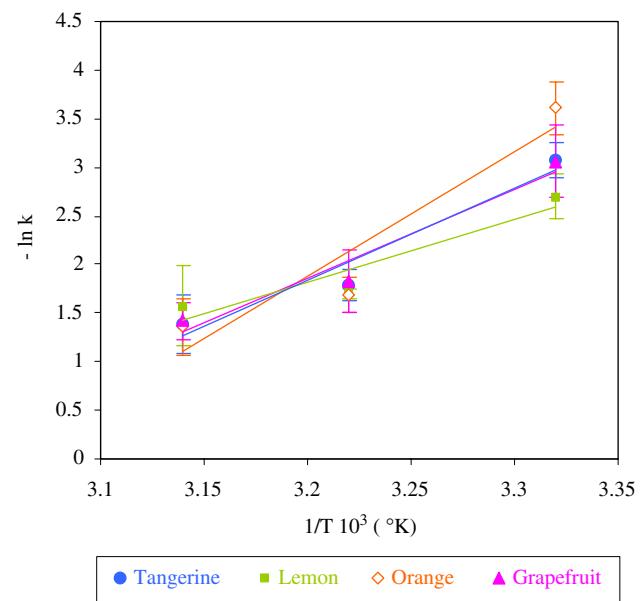


Fig. 2. Arrhenius plots of ascorbic acid degradation in citrus juice concentrates.

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	$E_a \pm SD$ (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
Orange	28	1.13	1.13	1.13	1.51	1.88	2.63	2.64	2.64
	37	1.13	10.57	30.58	90.25	141.99	270.39	358.38	493.58
	45	1.13	38.51	152.19	352.71	655.96	1138.20	1449.00	1945.60
Lemon	28	0.37	5.28	8.68	12.83	19.25	25.30	24.50	29.07
	37	0.37	42.67	86.10	157.47	233.76	460.35	423.33	526.05
	45	0.37	112.91	231.87	393.50	538.14	889.72	1024.90	1190.00
Grapefruit	28	2.64	4.90	8.30	12.46	16.99	26.05	26.05	28.32
	37	2.64	45.31	134.44	229.98	421.45	608.00	783.61	994.33
	45	2.64	131.04	336.85	745.84	1158.60	1864.80	2355.70	3252.30
Tangerine	28	0.37	0.37	1.13	1.51	2.26	2.64	2.79	2.79
	37	0.37	10.95	39.27	101.58	164.27	294.93	357.25	460.34
	45	0.37	36.25	161.25	396.52	681.26	1131.00	1604.20	2348.20

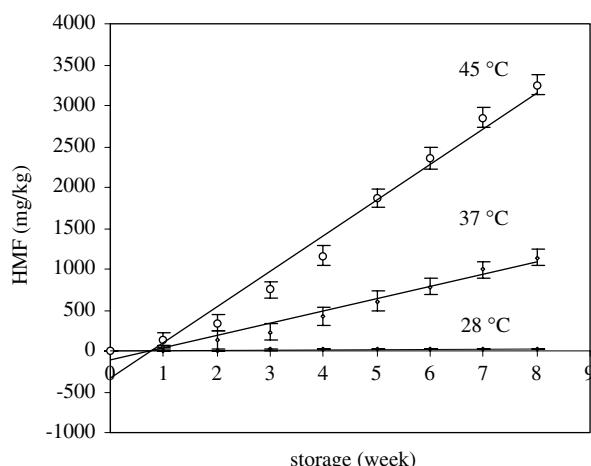


Fig. 3. HMF accumulation in grapefruit juice concentrates during storage.

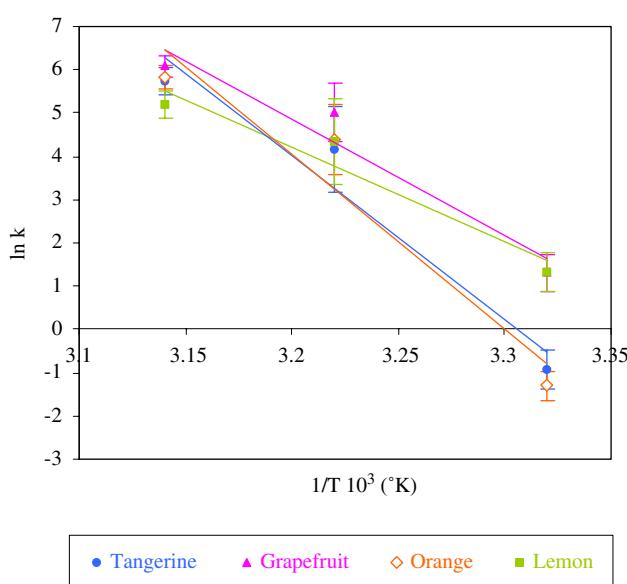


Fig. 4. Arrhenius plots of HMF accumulation in citrus juice concentrates.

#### 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.

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