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Degradation of Ascorbic Acid in Ethanolic Solutions

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ABSTRACT: Ascorbic acid occurs naturally in many wine-making fruits. The industry also uses ascorbic acid as an antioxidant and color stabilizer in the making of alcoholic beverages including white wine, wine cooler, alcopop, and fruit liqueur. However, the degradation of ascorbic acid itself may cause browning and the deterioration of color quality. This study was aimed to monitor the degradation of ascorbic acid, the formation of degradation products, and the browning in storage of ascorbic acid containing 0−40% (v/v) ethanolic solutions buffered at pH 3.2 as models of alcoholic beverages. The results show that ascorbic acid degradation in the ethanolic solutions during storage follows first-order reaction, that the degradation and browning rates increase with the increase of ethanol concentration, that the activation energy for the degradation of ascorbic acid is in the range 10.35−23.10 (kcal/mol), that 3-hydroxy-2-pyrone is an indicator and a major product of ascorbic acid degradation, and that aerobic degradation pathway dominants over anaerobic pathway in ascorbic acid degradation in ethanolic solutions.

KEYWORDS: *ascorbic acid, degradation, kinetics, ethanol, wine, browning*

INTRODUCTION

Ascorbic acid is among the major natural nutritional components that widely exist in fruits. In aqueous systems, ascorbic acid is very unstable and easily degraded in aerobic or anaerobic pathway.[1] The major factors that affect the stability of ascorbic acid in the processing and storage of fruit juice include oxygen, temperature, pH value, water activity, light, ionic strength, and sugar species.[2−13]

In the presence of oxygen, ascorbic acid loses electrons and hydrogen ions to form the unstable intermediate compound dehydroascorbic acid as the first step of degradation. Dehydroascorbic acid is quickly hydrolyzed to 2,3-diketo-L-gulonic acid, which is then decarboxylated into L-xylosone. L-Xylosone is further converted into other carbon compounds as the degradation products of ascorbic acid.[13] These degradation compounds may interact with food ingredients to cause browning, the alteration of flavor, and the reduction of product quality.[14] Shinoda et al. monitored ascorbic acid degradation and browning in a model solution of orange juice.[15,16] They concluded that furfural, 2-furoic acid, 5-hydroxymaltol, 3-hydroxy-2-pyrrone (3OH2P) and hydroxymethylfurfural (HMF) are the major degradation products; that 3OH2P and furfural are browning contributors; and that 3OH2P can be an indicator of ascorbic acid degradation in the aqueous system.

Numerous reports are relevant to the degradation of ascorbic acid in aqueous food while much fewer literatures have dealt with it in aqueous-ethanolic systems. Fruit liqueur, wine cooler, and alcopop are among the alcoholic beverages that may contain a noticeable amount of ascorbic acid originated from fruit or fruit juice as a raw material or ingredient in the manufacturing process.[17] Ascorbic acid may also be used in white wine industry as an antioxidant for the prevention of browning.[18−20]

Alcoholic beverages vary in their ethanol contents, or ethanol/water ratios. Different ethanol/water ratios constitute different chemical environments.[21,22] Jeney-Nagymate and Fodor found better retention of ascorbic acid in orange juice as compared with those in wine, and attributed it to the difference in chemical-physical characteristics between juice and alcoholic beverages.[9] Ethanol concentration has been recognized as a major factor that affects Maillard reaction mechanism and browning rate, chlorophyll stability, and the browning rate in ascorbic acid-catechin solutions.[23−26]

Chuang et al. constructed ethanolic solutions containing ascorbic acid and catechin to model for alcoholic beverages containing both ascorbic acid and phenolic compounds.[26] They reported that an increase in ethanol concentration in the model solutions accelerated ascorbic acid degradation and 3OH2P formation while decelerated browning, and suggested that 3OH2P may not be a good indicator of browning in the aqueous-ethanolic system containing ascorbic acid and catechin. They also postulated that the acceleration in browning is resulted from the reaction between catechin and L-xylosone, the intermediate product of aerobic ascorbic acid degradation.

In alcoholic beverages, ascorbic acid and phenolic compounds are usually present together. In such an environment, ascorbic acid may degrade following either its own pathway or a pathway involving its reaction with phenolic compounds. Presumably, the former may prevail in alcoholic beverages containing an overwhelmingly higher amount of ascorbic acid as compared with that of the active phenolic compounds. Knowledge pertaining to the degradation of ascorbic acid in aqueous-ethanolic system in the absence of phenolic compounds would be helpful in composing the complete scheme of browning in alcoholic beverages. The present study was therefore initiated.

MATERIALS AND METHODS

Chemicals. Ascorbic acid and potassium dihydrogen phosphate were purchased from Sigma Chemical Co. (St. Louis, MO). Furfural and 2-furoic acid were from Chem Service, Inc. (West Chester, PA),

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and 3-hydroxy-2-pyrone (3OH2P) from Tyger Scientific, Inc. (Ewing, NJ). Glacial acetic acid was from J. T. Baker Co. (Phillipsburg, NJ). Acetonitrile (gradient grade), methanol (gradient grade), and *ortho*-phosphoric acid (85%) were from Merck Co. (Darmstadt, Germany).

Preparation of Model Solutions. Aqueous and ethanolic (5, 10, 20, 30, 40%, v/v) model solutions containing ascorbic acid (40 mg/100 mL) were prepared. Wine cooler is the major item to be modeled after in the present study. The ascorbic acid content in commercial fruit juices is usually no higher than 43 mg/100 mL.[27] Wine cooler is commonly formulated with neutral spirit, fruit juice and water to reach an ethanol concentration between 3% and 5%. The ascorbic acid concentration in wine cooler is usually no higher than 40 mg/100 mL. It is therefore chosen as the concentration of ascorbic acid in the model solutions.

The pH of the solution was adjusted to 3.2, which is a common pH value of white wine, with 1.0 and 0.1 N hydrochloric acids by using a pH-Stat (PHM 290, Radiometer Analytical SAS, Lyon, France). Each 4.0 mL aliquot of the solution was filled into a 4.5 mL brown glass vial. The vial was sealed with Teflon gasket and capped. The model solutions were incubated at 25, 35, or 45 °C up to 35 days, and sampled periodically during storage for analysis.

Assessment of Browning. The absorbance at 420 nm of each sample was monitored as the browning index, using a UV−visible spectrophotometer (Model Helios Alpha, Spectronic Unicam, Cambridge, U.K.).

HPLC Analysis. The samples were then subjected to HPLC analysis referring to Shinoda et al. and Nour et al. with modifications.[15,28] Ascorbic acid and three major degradation products (furfural, 2-furoic acid, and 3OH2P) were analyzed using a 250 mm × 4.6 mm inside diameter, 5 μm particle size, Hypersil Gold C18 reversed-phase high pressure liquid chromatography (HPLC) column (Thermo Scientific, Waltham, MA). The HPLC analysis was run with a Prominence liquid chromatography system (Shimadzu, Kyoto, Japan) comprising a vacuum degasser, LC-20AT pump, SIL-20A autosampler and SPD-M20A diode array detector (DAD). The mobile phase for the determination of ascorbic acid was 50 mM potassium dihydrogen phosphate solution, of which the pH value had been adjusted to 2.8 with phosphoric acid. For the detection of degradation products, 50 mM acetic acid/acetonitrile (98:2 v/v) solution was chosen the mobile phase instead. The mobile phase was vacuum-degassed, and then set at 0.7 mL/min flow rate for all the chromatographic separations. The detection wavelength was set at the maximum optical absorbance, 244 nm for ascorbic acid, 254 nm for 2-furoic acid, 283 nm for furfural, or 300 nm for 3OH2P. Standard curves were established with analytical grade ascorbic acid, furfural, 2-furoic acid and 3OH2P. The injection volume was 20 μL for each sample. The HPLC analysis was supplemented with internal calibration by using the standard compounds. The degradation ratio of ascorbic acid was calculated employing the following equation,

$$\text{Degradation ratio } (\%) = [(A - B)/A]^{*}100$$

where A is the initial concentration of ascorbic acid, and B is the detected concentration of ascorbic acid.

Evaluation of Ascorbic Acid Degradation Kinetic Parameters. The changes in ascorbic acid content in the model solutions in storage were fitted into the first-order kinetics equation,

$$\ln(C/C_0) = -kt$$

for evaluating the rate constant k, in day^{-1}, for ascorbic acid retention. C and C_0 are the ascorbic acid contents at time t and time zero, respectively. C/C_0 expresses the % retention of ascorbic acid.

The temperature dependence of ascorbic acid retention was determined by Arrhenius equation:

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

where E_a is the activation energy (kcal mol^{-1}), R is the universal gas constant (1.987 cal mol^{-1} K^{-1}), T is the absolute temperature (K), and k_0 is the pre-exponential factor.

Statistical Analysis. Each experiment was performed in triplicate. The results were expressed in mean ± standard error. One-way analysis of variance (ANOVA) was used to analyze the variance among samples. Duncan's new multiple range test, at $p < 0.05$, was used to determine the significance of differences among sample means.

RESULTS

Kinetics of Ascorbic Acid Degradation. *1. Reaction Order.* Ascorbic acid retention in the pH 3.2 ethanolic solutions at 0−40% (v/v) ethanol concentrations and 25−45 °C storage temperatures is shown in Figure 1. The rate of ascorbic acid degradation was found to increase with the increase in ethanol concentration, incubating temperature, and storage time. At 45 °C storage, ascorbic acid is completely degraded in 8 days.

The semilogarithmic plot of the ascorbic acid retention (C/C_0) versus time reveals that the degradation of ascorbic acid in 0−40% ethanolic solutions follows the first-order reaction kinetics (Figure 2).

2. Rate Constant and Half-Life. Table 1 shows the rate constants of ascorbic acid degradation in the ethanolic model solutions incubated at various temperatures. The rate of degradation increases with the increase in the storage temperature and the ethanol concentration. An especially big increase occurred when the ethanol concentration was increased from 30 to 40% (v/v).

Half-life, calculated as $-\ln 0.5k^{-1}$, is defined as the time needed for 50% reduction in the concentration of substrate. A longer half-life corresponds with a slower degradation rate. The half-life of ascorbic acid in model solutions in storage at a fixed temperature is shortened when the ethanol concentration is increased (Table 1).

3. Activation Energy. The slope of the semilogarithmic plot of the rate constant versus the inverse of temperature depicts the activation energy (Figure 3). Ascorbic acid has the lowest value of activation energy at 10.35 kcal mol^{-1} in 40% (v/v) ethanol among all the tested ethanol concentrations (Table 1).

Degradation Products of Ascorbic Acid. HPLC DAD analysis found 2-furoic acid and 3OH2P in the ethanolic solution incubated at 45 °C (Figure 4). Furfural, which is another commonly recognized major degradation product of ascorbic acid in fruit juice, was not detected.

Both the contents of 2-furoic acid and 3OH2P increased with the increase in storage time (Figure 4). At the end of storage test, the contents of 2-furoic acid in all the model solutions at different ethanol concentrations were less than 10 ppm while those of 3OH2P ranged between 30 and 60 ppm. Restated, the compound 3OH2P is much more abundant than 2-furoic acid as an end product of ascorbic acid degradation in the ethanolic solutions. An increase in ethanol concentration accelerated the formation of both 3OH2P and 2-furoic acid. The formation of 3OH2P and 2-furoic acid in various concentrations of ethanol was found to follow zero-order kinetics with a determination coefficient of correlation in between 0.75−0.90 and 0.94−0.98, respectively.

Browning in Ethanolic Model Solutions. Figure 5 shows the progress of browning in ethanolic solutions of ascorbic acid at 45 °C for 35 days as an accelerated storage test. All the samples browned readily. The browning rate increased with the increase in ethanol concentration. The model solution at 40% (v/v) ethanol concentration browned more seriously than all other samples at lower ethanol concentrations.

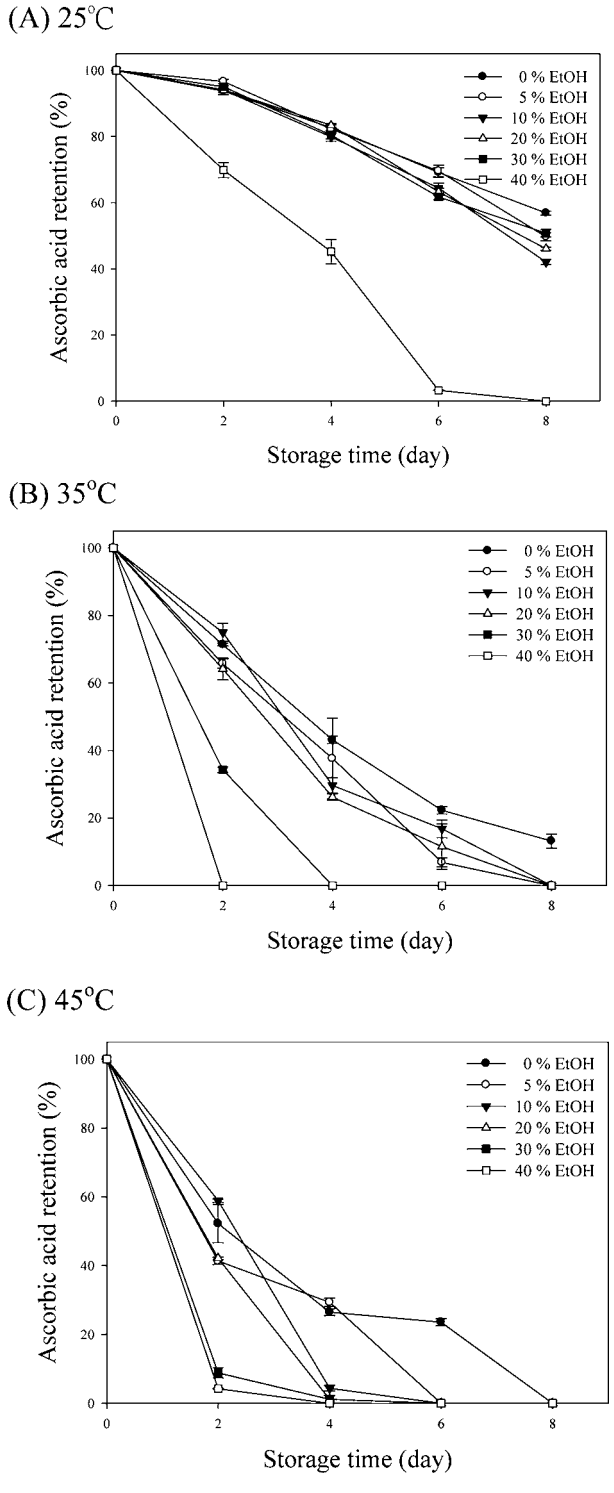

Figure 1. Retention of ascorbic acid in the model solutions (40 mg/100 mL, pH 3.2) during storage at various temperatures.

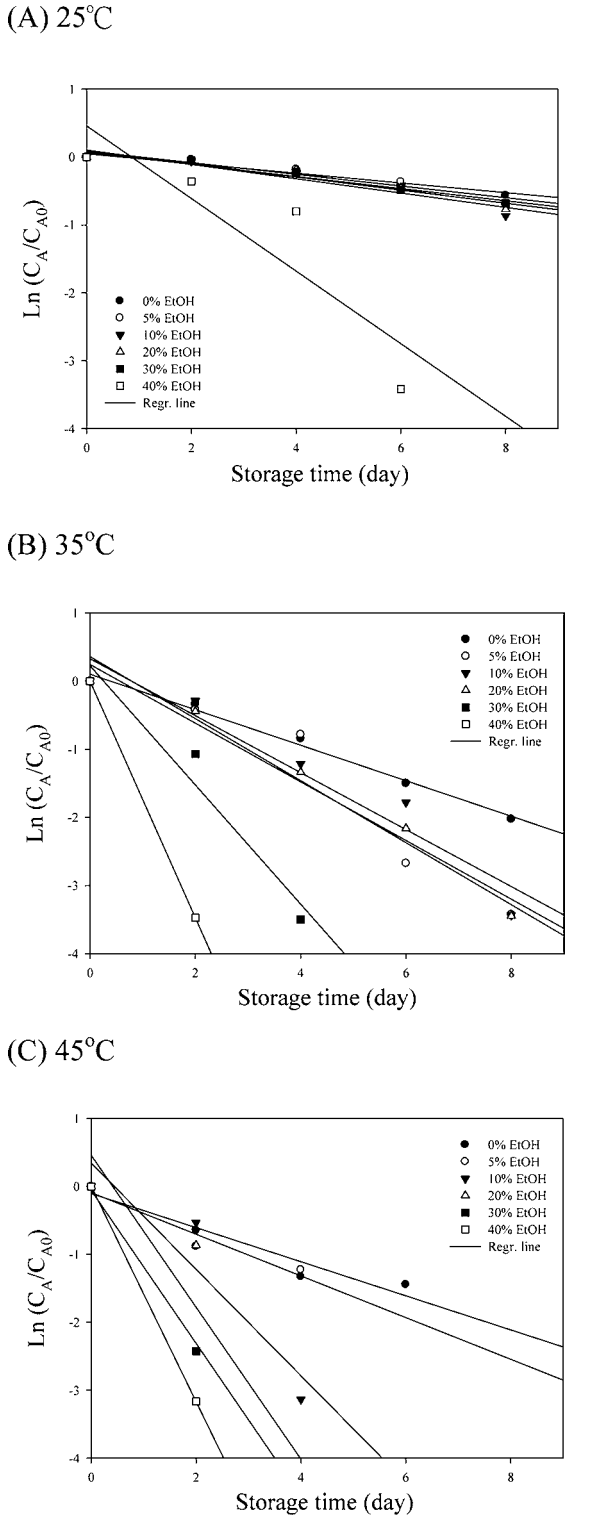

Figure 2. First-order kinetics plots of ascorbic acid degradation in the model solutions (40 mg/100 mL, pH 3.2) during storage at various temperatures.

DISCUSSION

Reaction Kinetics. Researchers found different chemical kinetics of ascorbic acid degradation during storage in different aqueous systems. Among them, zero-order reaction kinetics in an intermediate moisture model food system, pseudo-first-order in dehydrated guava fruit, first-order in orange juice and citrus juice concentrates, and second-order in lemon juice all have been reported.[5,6,10,29,30] However, no literature in regard to the degradation kinetics of ascorbic acid in ethanolic systems is available yet. Normal white wine contains approximately 12% (v/v) ethanol with a pH value between 3.0 and 3.5.[31] Wine cooler and alcopop usually contain ethanol in the ranges of 4−6% (v/v) and 5−12% (v/v), respectively.[17,32] Ascorbic acid may also be present in fruit liqueurs, which normally contain ethanol no higher than 40% (v/v). The present study evaluated ascorbic acid degradation in 0−40% (v/v) ethanolic model

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Table 1. Effect of Ethanol Concentration on the Rate Constant (k), Half-Life ($t_{1/2}$), and Activation Energy (E_a) of Ascorbic Acid Degradation in Model Solutions (40 mg/100 mL, pH 3.2)

ethanol concentration (v/v)	temperature (°C)	rate constant (day^{-1})	$t_{1/2}$ (day)	E_a (kcal/mol)
	45	0.261 ± 0.007	2.66	12.29
0%	35	0.251 ± 0.005	2.76	
	25	0.072 ± 0.005	9.69	
	45	0.455 ± 0.005	1.52	15.79
5%	35	0.307 ± 0.012	2.26	
	25	0.086 ± 0.002	8.08	
	45	0.783 ± 0.010	0.89	20.52
10%	35	0.418 ± 0.002	1.66	
	25	0.089 ± 0.001	7.76	
	45	1.117 ± 0.010	0.62	23.10
20%	35	0.431 ± 0.001	1.61	
	25	0.096 ± 0.002	7.19	
	45	1.125 ± 0.043	0.62	22.46
30%	35	0.875 ± 0.004	0.79	
	25	0.105 ± 0.001	6.58	
	45	1.583 ± 0.001	0.44	10.35
40%	35	1.737 ± 0.050	0.40	
	25	0.535 ± 0.002	1.30	

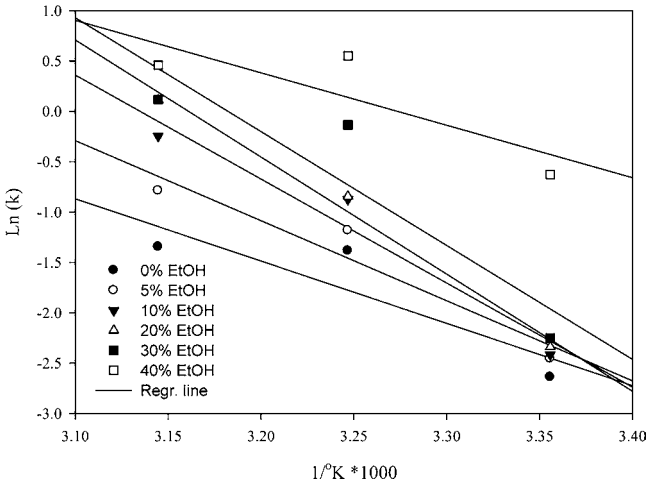

Figure 3. Arrhenius plot for ascorbic acid degradation in the model solutions (40 mg/100 mL, pH 3.2).

solutions buffered at pH 3.2, simulating alcoholic beverages with fruit as a raw material, and found that the degradation follows first order reaction kinetics with temperature-dependency (Figure 2).

Effect of Ethanol Concentration. Chuang et al. reported that a higher ethanol concentration corresponds to a higher degradation rate of ascorbic acid in ascorbic acid−catechin model solutions.[26] They postulated that a higher ethanol concentration provides a lower water activity environment and promotes the dehydration of ascorbic acid degradation intermediate compound L-xylosone, therefore, exhibits an increased rate of ascorbic acid degradation. In the present study, the rate of ascorbic acid degradation in ethanolic solutions at a fixed temperature was also found to increase with the increase in ethanol concentration (Table 1). Our findings are supportive to the above-mentioned postulation. Ethanol concentration can be an important parameter for ascorbic acid retention in alcoholic beverages.

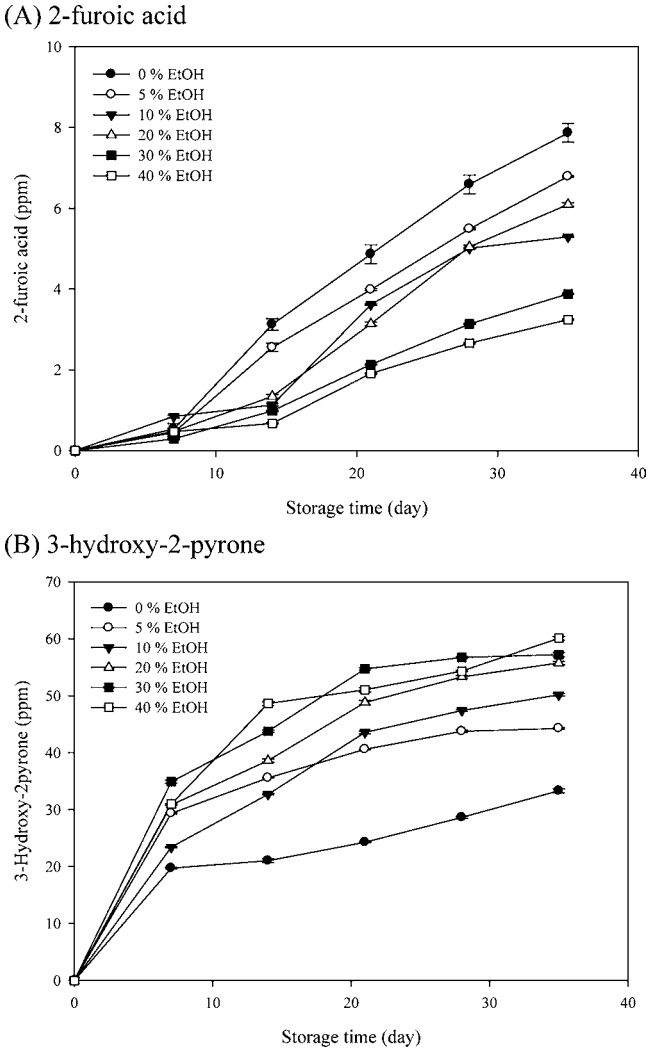

Figure 4. Formation of 2-furoic acid and 3-hydroxy-2-pyrone in the model solutions of ascorbic acid (40 mg/100 mL, pH 3.2) during storage at 45 °C.

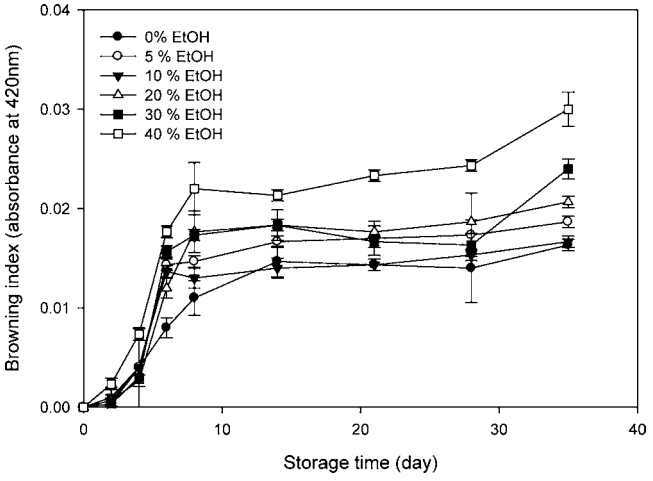

Figure 5. Browning in the model solutions of ascorbic acid (40 mg/100 mL, pH 3.2) during storage at 45 °C.

Temperature Effect. Results from the present study show that temperature is another important factor for the stability of ascorbic acid. A higher storage temperature resulted in a higher

degradation rate of ascorbic acid in the ethanolic model solutions (Table 1). Burdurlu et al. reported that storage temperature affected degradation rate of ascorbic acid in orange juice concentrate with a pH value at 3.2. In their samples, the degradation rate of ascorbic acid at 45 °C was approximately 9 times that at room temperature.[6] In the present study, the degradation rate of ascorbic acid in 40% (v/v) ethanolic model solution at 45 °C was approximately 3 times that at room temperature. The effect of temperature on the degradation rate of ascorbic acid is obvious in ethanolic solutions, although not as strong as that in orange juice concentrate. Ascorbic acid in all the ethanolic model solutions degrades over 99% in 45 °C storage for 8 days (Figure 2). On the basis of the rate constants, we predict that a similar degree of ascorbic acid degradation in 25 and 35 °C storages would occur in approximately 54 days and 15 days, respectively.

Villota and Hawkes concluded that the activation energy of ascorbic acid degradation ranges from 5 to 40 kcal/mol in aqueous systems.[33] The values of activation energy of ascorbic acid degradation are 30 and 25.16 kcal/mol in orange juice and orange juice concentrate, respectively.[6,29] The present study found that the values of activation energy for ascorbic acid degradation in 0−40% (v/v) ethanol concentrations are between 10.35 and 23.10 kcal/mol (Table 1), within the range for reported values in aqueous systems. The model solution at 40% (v/v) ethanol concentration is characterized with the lowest value of activation energy, 10.35 kcal/mol. A change in storage temperature exerts a heavier impact on the degradation rate of ascorbic acid at this ethanol concentration as compared with other concentrations.

Degradation Pathway and Browning. Yuan and Chen reported that 3OH2P, 2-furoic acid and furfural are the major degradation products of ascorbic acid in acid aqueous solution.[14] Shinoda et al. found 3OH2P and 2-furoic acid as the two major degradation products of ascorbic acid in orange juice model solution.[15,16] Chuang et al. found 3OH2P and 2-furoic acid in ascorbic acid−catechin ethanolic model solutions.[26] These two degradation products were found in the present study (Figure 4).

There are aerobic and anaerobic pathways for the non-enzymatic degradation of ascorbic acid. The end-products 3OH2P and 2-furoic acid are formed in the aerobic degradation, whereas furfural is formed in the anaerobic degradation.[14] In the present study, 3OH2P and 2-furoic acid were found in all the ethanolic model solutions while furfural was never detected, indicating the predominance of aerobic pathway over anaerobic pathway in the degradation of ascorbic acid in ethanolic solutions.

Between the two major aerobic degradation products of ascorbic acid, 3OH2P and 2-furoic acid, only the former causes browning.[15,16] The present study found 3OH2P a major degradation product of ascorbic acid in the ethanolic model solutions (Figure 4). An increase in ethanol concentration in the model solutions accelerates 3OH2P formation and browning (Figure 5). The browning index correlates well with the concentration of 3OH2P (coefficient of determination, $R^2 = 0.93$) in linear regression. The roles of 3OH2P in ascorbic acid degradation and browning appear similar between aqueous and aqueous-ethanolic systems.

In the aerobic degradation pathway of ascorbic acid, L-xylosone may be converted to brown-colored 3OH2P.[13] L-Xylosone is also the only intermediate product in aerobic degradation of ascorbic acid that may react with catechin and form brown-colored xanthylium cation pigments.[34] Chuang et al. reported that an increased ethanol concentration in ascorbic acid−catechin model solutions accelerated ascorbic acid degradation and 3OH2P formation but decelerated browning.[26] They postulated that an increase in ethanol concentration in their model solutions promotes more L-xylosone to dehydrate and form 3OH2P, while it leaves less to react with catechin and form xanthylium cation pigments. Assuming the color intensity of 3OH2P is lower than that of xanthylium cation pigments, deceleration in browning of the solution would occur. The present study found that an increase in ethanol concentration in the ascorbic acid model solutions promoted the accumulation of 3OH2P and accelerated browning (Figure 5). We postulate that the ethanolic model solutions in the present study contained no catechin to react with L-xylosone to form xanthylium cation pigments; therefore, any accelerated formation of 3OH2P in the system would simply be reflected with more browning.

On the basis of the above-described findings, we propose that 3OH2P can be an indicator of browning in ethanolic model solutions containing ascorbic acid only. It may also be true in alcoholic beverages containing an overwhelmingly higher amount of ascorbic acid as compared with the amount of browning-active phenolic compounds.

Further studies, including the purification and identification of the browning products, to elucidate the detailed mechanism of the ascorbic acid browning reaction in ethanolic solutions are recommended. Ascorbic acid and phenolic compounds are usually present together in alcoholic beverages. Ascorbic acid may degrade in its own pathways or following a pathway that involves the reaction with phenolic compounds. Experiments in the real systems to evaluate the relative importance of each pathway are also recommended.

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Notes

The authors declare no competing financial interest.

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