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Study on the Kinetics of Vitamin C Degradation in Fresh Strawberry Juices

Lanny Sapei[a,]* and Lie Hwa[a]

[a]*University of Surabaya, Raya Kalirungkut, Surabaya 60293 East Java, Indonesia*

Abstract

Vitamin C is an essential nutrient needed for maintaining the human health. Strawberry fruit have a relatively high content of vitamin C, which is around 40-70 mg/ 100 g strawberries. However, vitamin C which is also known as ascorbic acid is easily degraded during storage. The objective of this research is to study the kinetics of degradation of vitamin C in fresh strawberry juices upon storage and to investigate the effect of storage temperatures and sugar addition on the ascorbic acid loss in strawberry juices. Four different types of fresh strawberry juices were prepared, namely A, B, C, and D. Juices A and C were stored at a room temperature of 28^{o}C, while samples B and D were stored at a refrigerated temperature of 8°C. Furthermore, juices A and B were prepared without sugar addition, while sugar was added to juices C and D. The concentration of ascorbic acid in the juice was analyzed using iodimetric titration method. It was monitored every one hour for 8 hours of storage for the kinetics of ascorbic acid degradation study. The results showed that the degradation reaction of vitamin C followed zero-order kinetic models in all types of juices. The degradation reaction rate constants obtained for juices A, B, C, and D were 4.42; 3.63; 2.32; and 1.85 mg vitamin C/(100 ml. h), respectively. The activation energy for the vitamin C degradation in fresh strawberry juices with sugar and without sugar addition was estimated to be 1.90 kcal/ mol and 1.65 kcal/ mol, respectively. In conclusion, the storage at a lower temperature combined with sugar addition could effectively slow the rate of degradation of vitamin C.

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Keywords: kinetics; strawberry juices; vitamin C; degradation

* Corresponding author. Tel.: +62-31-2981150; fax: +62-31-2981151
E-mail address: lanny.sapei@ubaya.ac.id

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1. Introduction

Vitamin C or ascorbic acid is water-soluble vitamin and is very essential to human beings[1]. Vitamin C also functions as an effective antioxidant that is required to maintain human health[2,3]. Nowadays, there is an increasing demand of nutritious food thus there have been many attempts to maximize the nutrients retention in both processing and storage of the foods. Vitamin C is usually considered as the nutrient quality indicator during processing and storage of foods since it is generally observed that, if ascorbic acid is well retained, the other nutrients are also well retained[1].

Vitamin C is mainly found in vegetables and fruits[3]. Amongst the fruits, strawberries are considered to be one of most rich in ascorbic acid[3,4]. The vitamin C content in fresh strawberries is up to 80 mg/100 g [3]. Strawberries could be easily processed into strawberry juices as convenient sources of ascorbic acid for human consumption. However, ascorbic acid of fruit juices is generally readily oxidised and lost during the storage. There are many factors influencing this oxidation process, such as light exposure, pH[5], level of dissolve oxygen[5], metal ions presence[6], sugar presence[7], and storage temperature[1,5,8,9]. Furthermore, ascorbic acid is thermo-labile and highly sensitive to various processing conditions[10].

The degradation of ascorbic acid upon storage is the main problem of nutritional quality loss in strawberry juices which also determine their shelf life. This fact is of great importance to the juice manufacturers to properly process and store the juice under appropriate conditions, thus the consumer would get the maximum benefit of the vitamin C content in the juices. It is necessary to understand the ascorbic acid degradation reaction by investigating the kinetics of ascorbic acid loss in strawberry juices during storage. The kinetic order and rate constant are the basic requirement to define shelf life of fruit juices. Furthermore, kinetic models can be used not only for objective, fast and economic assessments of food quality[10], but may also be employed to predict the influence of several experimental variables on critical nutritional values. Different kinetic studies in literatures have tried to estimate the rate constants for the degradation of vitamin C in fruit juices. Several kinetic models such as zero-order[11], first order[8], pseudo-first order[1], and second order kinetic reactions[12] have been successfully used to describe vitamin C degradation. However, there are only few studies on kinetics of ascorbic loss in strawberry juices during storage. The aim of this study is to evaluate the kinetics of degradation of vitamin C in freshly home-made strawberry juices upon 8 hour storage at a room temperature and at a refrigerated temperature besides investigating the effect of storage temperatures and sugar addition on the vitamin C loss in strawberry juices. Direct iodimetric titration was used to evaluate the vitamin C content in strawberry juices. This method is simple, reliable and cost effective in terms of the instrumentation and reagents.

2. Materials and Methods

2.1. Reagents

Ascorbic acid p.a., I_2 0.01 N, KIO_3 0.1 N, $Na_2S_2O_3$ 0.1 N, KI 10%, H_2SO_4 2N, 1% starch solution, and distilled water.

2.2. Fruit materials

Fresh strawberries were purchased from the local supermarket of Surabaya, East Java, Indonesia. The fruit leaves were removed out, followed by washing prior to blending.

2.3. Juice preparation

Clean fresh strawberries of about 240 g were cut into smaller pieces, followed by blending in a blender (Phillips E2371, Indonesia). The resulting strawberry pulp was then filtered to separate the solid residues from the liquid concentrates. The liquid concentrates were then diluted by the addition of mineral water (1 : 4 v/v) in order to obtain fresh strawberry juice. Four types of fresh strawberry juices were prepared namely juices A, B, C, and D. Juices A and B were prepared without sugar addition, while sugar (5.5% w/v) were added into juices C and D. Juices A and C were stored at a room temperature of 28°C, whereas juices B and D were kept at a refrigerated temperature of 8°C. No any preservatives were added to the juices and no thermal treatments applied to the juices. All juices were kept in closed glass containers.

2.4. Determination of Vitamin C

Vitamin C content in the fresh strawberry juices was determined using a direct iodimetric titration. An aliquot of 25 ml of a fresh strawberry juice were placed in a 250 ml erlenmeyer flask and then 2 ml of starch indicator was added. Samples were titrated with 0.01 N iodine solutions which were previously standardized with sodium thiosulfate in the matrix of potassium iodide. Prior to using, the sodium thiosulfate solution was standardized with a primary standard solution of potassium iodate in acidic environment. A blank titration was performed prior to titration of each sample (n = 4). Each ml of 0.01 N iodine is equivalent to 0.8806 mg ascorbic acid[13]. Results were calculated as mg of L-ascorbic acid per 100 ml of orange juice. Each sample was prepared and analysed in duplicate.

2.5. Data Analysis

Vitamin C in the fresh strawberry juices were determined for the first 8 hours of storage right after the preparation with an interval of 1 hr, considering the fact that the juices especially stored at 28°C were not acceptable organoleptically anymore upon the storage beyond 8 hours.

The degradation of ascorbic acid in fresh strawberry juices upon storage would be evaluated using zero-order (Eq. 1) and first-order kinetic models (Eq. 2). The most appropriate model was selected based on the correlation coefficients (R^2) calculated using the least square procedure.

$$C = C_o - k_0 t \quad (1)$$

$$C = C_o.\exp(-k_1 t) \quad (2)$$

with C the ascorbic acid (AA) concentration (mg AA/100 ml juice) at time t, C_o the ascorbic acid concentration at time 0, k_0 and k_1 the ascorbic acid degradation rate constant for the zero order (mg AA/(100 ml juice. hour)) and for the first order (per hour), respectively, t the storage time (hours).

Half-life ($t_{1/2}$) of vitamin C is the estimated time where the concentration of ascorbic acid is decreased by 50% from its initial value ($C = 0.5\ C_o$). Half-life of each strawberry juice at its corresponding temperature storage is determined using the kinetic models (Eq. 1 or Eq. 2) depending on the best fitted model to the experimental data.

The temperature dependence of the ascorbic acid degradation can be expressed in terms of the activation energy (E_a) and adequately described by Arrhenius kinetics (Eq. 3), where k_A and k_B are the ascorbic acid loss rate at storage temperatures of T_A (28°C) and T_B (8°C), respectively. E_a is the activation energy for the ascorbic acid degradation (kcal/ mol), R is the universal gas constant (1.987 cal/ mol. K) and T is the absolute temperature (K).

$$k_A = k_B.\exp\left[-\frac{E_a}{R}\left(\frac{1}{T_A} - \frac{1}{T_B}\right)\right] \quad (3)$$

3. Results and Discussion

The degradation of vitamin C in fresh strawberry juices was studied in terms of ascorbic acid (AA) concentration. During storage, ascorbic acid concentrations in all strawberry juices were gradually decreased with time at a rate depending on the storage temperature and sugar presence. The degradation of ascorbic acid in all strawberry juices fitted by zero-order and first-order kinetics models was depicted in Fig. 1 and Fig. 2, respectively. The kinetic parameters such as ascorbic acid loss rates together with their R^2 correlations obtained from the fitting using zero-order (Eq. (1)) and first-order (Eq. (2)) kinetic models can be seen in Table 1.

It turned out that the degradation of ascorbic acid in all fresh strawberry juices fitted best to the zero order kinetic models regardless of storage temperatures and sugar addition. The zero order rate constants were increased with the increase of storage temperature (juice A *vs.* juice B and juice C *vs.* juice D). In contrast, the rate constants were decreased almost in half upon sugar addition into the juices (juice A *vs.* juice C and juice B *vs.* juice D). The deterioration rate of vitamin C has been found to be maximum in juice A and the lowest in juice D. Ascorbic acid concentration decrease more rapidly at the beginning of storage due to the immediate reaction of an amount of ascorbic acid with the dissolved oxygen and afterward the ascorbic acid degraded more slowly[9,14]. Van Bree et.al.[11] found out that the degradation of ascorbic acid was successfully described by a zero order kinetic model for the oxygen concentrations lower than 0.63% and by a first order kinetic model for all oxygen concentrations. It seemed possible that in these freshly made strawberry juices, the rapid vitamin C degradation might occur during the first one hour following first-order kinetic model which was not monitored, followed by slower degradation rate according to zero order kinetic reaction model.

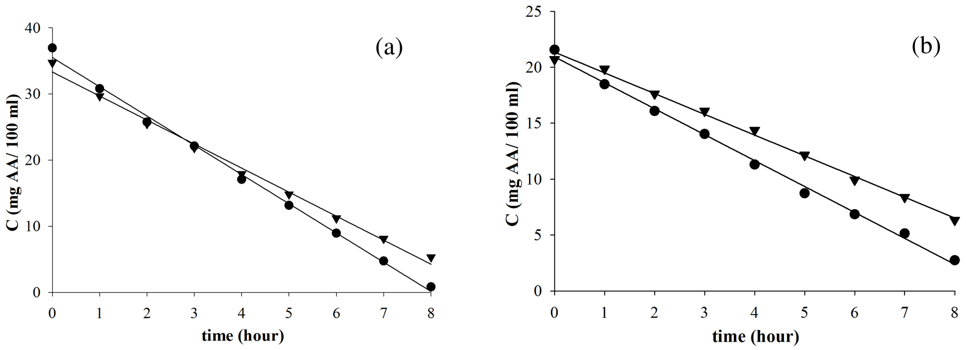

Fig. 1 Ascorbic acid degradation during storage at 28ºC and 8ºC of fresh strawberry juices prepared (a) without sugar (b) with sugar. The full lines represent the fitted zero-order kinetic models. (●) 28ºC; (▼) 8ºC.

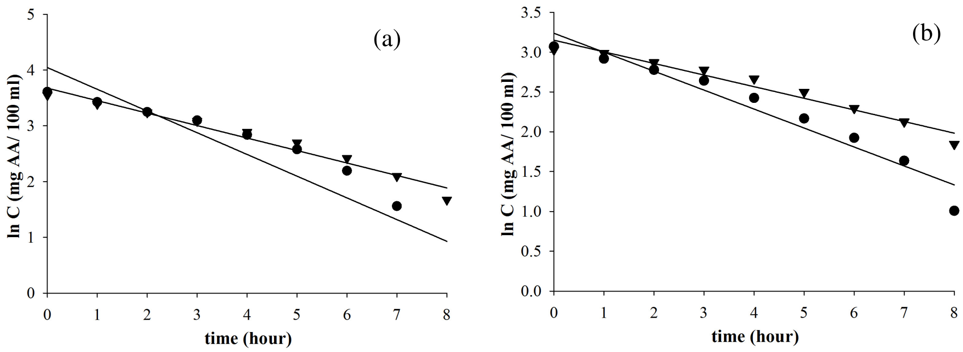

Fig. 2 Ascorbic acid degradation during storage at 28ºC and 8ºC of fresh strawberry juices prepared (a) without sugar (b) with sugar. The full lines represent the fitted first-order kinetic models. (●) 28ºC; (▼) 8ºC.

Table 1. Kinetic loss rates constants and R^2 values according to zero-order and first order kinetic models fitted to the experimental data of ascorbic acid concentrations in fresh strawberry juices prepared with and without sugar and stored at 28ºC and 8ºC.

			Zero Order			First Order	
Strawberry Juice	Storage Temperature (ºC)	Sugar	k_0 (mg AA/(100 ml.h))	R^2	$t_{1/2}$ (h)	k_1 (h^{-1})	R^2
A	28ºC	without sugar	4.419	0.996	4.180	0.390	0.809
B	8ºC	without sugar	3.631	0.994	4.782	0.224	0.965
C	28ºC	with sugar	2.319	0.995	4.646	0.238	0.943
D	8ºC	with sugar	1.854	0.995	5.597	0.146	0.959

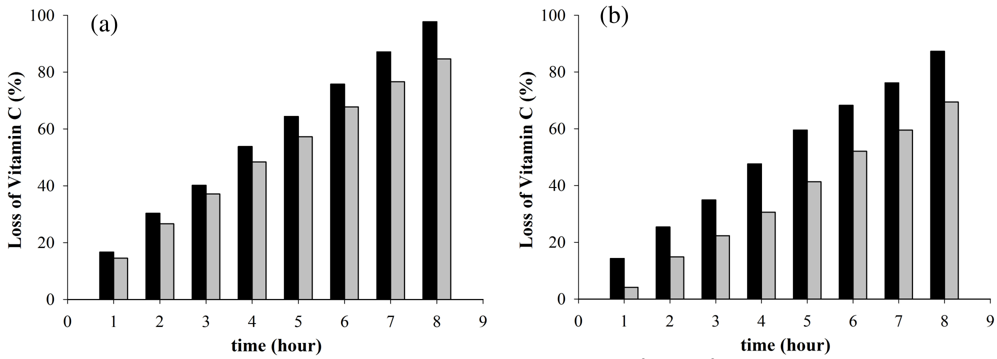

Fig. 3 Comparison of ascorbic acid loss in fresh strawberry juices stored at 28ºC and 8ºC and prepared (a) without sugar (b) with sugar. (■) 28ºC; ( ) 8ºC.

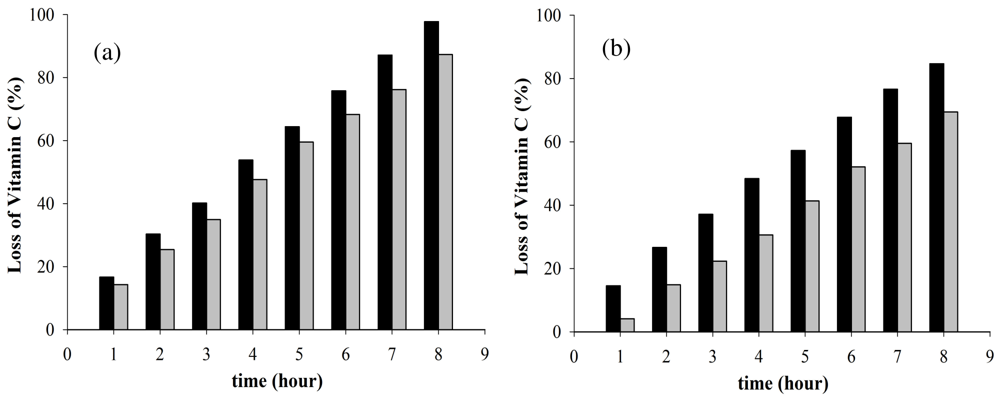

Fig. 4 Comparison of ascorbic acid loss in fresh strawberry juices with and without sugar addition stored at (a) 28ºC (b) at 8ºC. (■) without sugar, ( ) with sugar.

The effect of storage temperature on the ascorbic acid loss in the fresh strawberry juices could be clearly seen in Fig. 3. The ascorbic acid loss was decreased when the juice was stored at the refrigerated temperature. This was confirmed by the previous investigation that lower temperature storage could slow the degradation rate of vitamin C[1,5,8,9]. Furthermore, the ascorbic acid loss was decreased upon sugar addition (Fig. 4). This implies that the degradation rate of vitamin C in the fresh strawberry juices could be retarded simply by the addition of sugar as a common sweetening ingredient in fruit juices. This seemed plausible that the sugar presence would decrease the concentration of dissolved oxygen in the juice, thus the oxidation process of ascorbic acid was delayed. It has been reported that sucrose was able to inhibit ascorbic acid oxidation in a closed aqueous system[7]. Interestingly, storing the fresh strawberry juices at low temperature combined with sugar addition could significantly suppress the ascorbic acid loss (Fig. 3b and Fig. 4b). After 8 hours, the ascorbic acid loss in juice A reached almost 100% compared to that of only 70% in juice D. The strawberry juices especially stored at 28^{o}C were deteriorated and organoleptically unaccepted anymore beyond 8 hours of storage most probably due to the microbiological activity. Juice D had the longest half life of about 5.5 hours compared to juice A of which half time is about 4.2 hours (Table 1). All of these facts demonstrated a synergism effect between low temperature storage and the presence of sugar in order to effectively inhibit the degradation of vitamin C in fresh strawberry juices.

The activation energy of ascorbic acid degradation were estimated to be 1.65 kcal/ mol and 1.90 kcal/ mol for the fresh strawberry juices prepared without and with sugar, respectively. These values were far less compared with the E_a of about 6-10 kcal/ mol for ascorbic acid loss in strawberry juices investigated by Verbeyst *et.al.*[14]. This could be due to different processing and treatment of strawberry juices. There was thermal treatment involved during the preparation of strawberry juices described in Verbeyst *et.al.*[14] which was not applied in this work. Higher activation energy of the fresh strawberry juices prepared with sugar indicated a retarded rate of degradation of ascorbic acid, thus demonstrating the effectiveness of sugar addition for better vitamin C retention in the juices. This confirmed the previous work showing that the E_a of ascorbic acid oxidation in sucrose solution was greater in comparison to the E_a in the solution containing no sucrose[7].

The relatively low activation energy and short half life of ascorbic acids obtained from this work demonstrated the proneness of vitamin C in freshly home-made strawberry juices to a rapid degradation process. Based on this fact, the consumers should consider the decrease of nutritional content of vitamin C in the fresh strawberry juices upon storage.

4. Conclusion

The ascorbic acid content of fresh strawberry juices ranged from 20 to 40 mg/100 ml of juice. Vitamin C or ascorbic acid concentration in all strawberry juices were decreased with time upon storage. The degradation of vitamin C in all types of fresh strawberry juices was found to follow zero-order reaction kinetics. The degradation reaction rate constants were decreased when the juices were stored at the refrigerated temperature and also upon sugar addition. They ranged from 1.85 to 4.42 mg vitamin C/(100 ml. h), respectively. The ascorbic acid loss after 8 hour storage were found to be almost completely degraded in the juice stored at room temperature and without sugar addition, while in the juice stored at refrigerated temperature and with sugar addition the ascorbic acid loss could be suppressed to about 70%. The activation energy for the degradation reaction of vitamin C in fresh strawberry juices with sugar addition was higher compared to those prepared without sugar addition. The half-life of the strawberry juice with sugar presence and stored at the low temperature was the longest amongst the others. Storage at a refrigerated temperature and sugar addition could be used as a simple method for the preservation of freshly home-made strawberry juices. This kinetic study of vitamin C degradation in fresh strawberry juice would be useful for the consumers to get more insight on the decrease of nutritional quality of the juices upon storage, thus the health benefit of freshly made strawberry juices could be maximized prior to consumption.

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