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Prediction of Ascorbic Acid Stability in Powdered Beverage

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분말음료의 아스콜빈산 안정성 예측

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Abstract

A powdered beverage with afruit flavor was stored at 4, 21, 35 and 45°C for 180 days to study ascorbic acid destruction at the selected temperatures. Degradation of ascorbic acid in the model followed the first order reaction, and the temperature dependence of reaction rate constants at tested temperatures was accounted for by the Arrhenius equqtion. The calculated activation energy for the destruction of ascorbic acid was 3. 3 Kcal/mole. The relationship between ascorbic acid content and sensory flavor score of the beverage indicated that samples with destruction of ascorbic acid over 25% showed objectionable flavor.

An attempt was made to predict the quality of powdered beverage by using a simulation model. A comparision between ascorbic acid values from shelflife tests and the simulation program showed a good agreement within acceptable error. This result demonstrated that quality of powdered beverage could be predicted by using a computer simulation model with a desired accuracy.

Introduction

During the past several years, techniques were developed to predict the shelf life of packaged foods based on the kinetics of quality deterioration. Reviews of this subject were published recently by Karel & Riemer[1], Villota & Karel[2], Heldman & Singh[3], and Labuza.[4] The related subject of predicting nutrient retention during processing was summarized by Lund[5]. Quast & Karel[6] investigated the storage life of potato chips as a model of a dry food, which deteriorated by oxidation due to atmospheric oxygen and by textural changes due to pick-up of water. The approach to model building included a theoretical consideration of reaction kinetics, as well as empirical data fitting. A study of the prediction of nutrient stabil ity was carried out by Wanninger[7], who postulated a mathematical model of the rate of ascorbic acid degradation based on the chemistry of ascorbic acid. This theoretical model was verified and its applicability tested on data from the literature.

One of the most labile nutrients in foods is ascorbic acid and its stability has been used as an indicator of product quality. Acomprehensive review on its stability was presented by Bauernfeind and Pinkert[8]. Kirk *et al.*[9] studied the degradation of ascorbic acid in a model system as a function of water activity, moisture content, oxygen and storage temperature. In their study the rate of destruction of the vitmain was well described by the first order kinetics.

The purpose of this study was to establish a relationship between ascorbic acid contents and quality of powdered beverage, and to predict ascorbic acid stability in powdered beverage by a time-temperature model.

Materials and Methods

Material

A model system of powdered beverage was prepared by dry blending powdered fruit flavor, sugar, ascorbic acid and others in a ribbon blender (rpm; 50) for 15 mine. The composition of the system is shown in Table 1.

Blended beverage was filled in 200*g* jars, sealed and stored at the selected temperatures. Powdered beverage samples were taken at 20-day intervals to study the rate of ascorbic acid destruction and a relationship between that and product quality. 10~20*g* samples of powdered beverage were taken from 12 jars, blended and used for analysis.

Table 1. Compositions of powdered beverage model system

Composition	% (dry wt. basis)
Sugar	90.5
Fruit flavor	1.0
Ascorbic acid	0.5
Color Na-citrate Tricalaium phosphate CMC Citric acid	8.0
Total	100.0

Determination of ascorbic acid by HPLC

Ascorbic acid was determined by Haney's method [10], using high performance liquid chromatography (HPLC). Twenty grams of sample was dissolved in 150*ml* of 5% HPO_3 and filtered through Whatman No. 5 filter paper. The filterate was diluted 10 times with 5% HPO_3 and injected onto a reverse phase HPLC with μ-Bondapak/C_{18} column (Waters Associates Inc.). Ascorbic acid in powdered beverage was calculated by peak area. The operating conditions of HPLC are shown in Table 2.

Table 2. Operating conditions of HPLC

Instrument	Waters Associates, Model 440
Column	μ-Bondapak/C_{18}
Solvent	water; methanol; tetrabutyl ammonium phosphate ,96.5; 2.5; 1.0
Detector	UV 254*nm*
Flow rate	2.0*ml*/min
Attenuation	10
Injector	U 6 K
Chart speed	0.2in/min

Order of reaction with respect to ascorbic acid destruction

Powdered beverage with initial ascorbic acid concentration of 513*mg*/100*g* was stored at various temperatures for 180 days and samples were analyzed for ascorbic acid at 20-day intervals. A plot of logarithm of ascorbic acid concentration versus storage time was prepared and the rate constant of ascorbic acid destruction (K) was determined. The half-life of ascorbic acid in powdered beverage at 35°C was calculated by $T\frac{1}{2}=0.693/K$.

Effect of storage temperature

Powdered beverage was stored in temperature controlled storage chambers at 4°, 21°, 35° and 45°C. Pepresentative samples were analyzed for ascorbic acid at 20-day intervals, and rate constants and an activation energy (Ea) were calculated. All calculations in the study were made using an IBM system Model 4331 Group I Ao 2 at the Korean Information Computing Co. Ltd.

Sensory Evaluation

Samples were evaluated for flavor at the end of each storage period by 15 trained panel members. Samples for flavor evaluations were prepared by dissolving 20*g* of beverage powder in 150*ml* of cold water. At each storage period, panelists were asked to taste control and stored samples, and to record flavor scores on a score card.

Table 3. First-order rate constants determined at various storage temperature

Storage temp.	Rate constant K (day^{-1})	Correlation coefficient
3°C	1.305×10^{-3}	0.98
21°C	1.57×10^{-3}	0.99
35°C	2.099×10^{-3}	0.99
45°C	3.017×10^{-3}	0.99

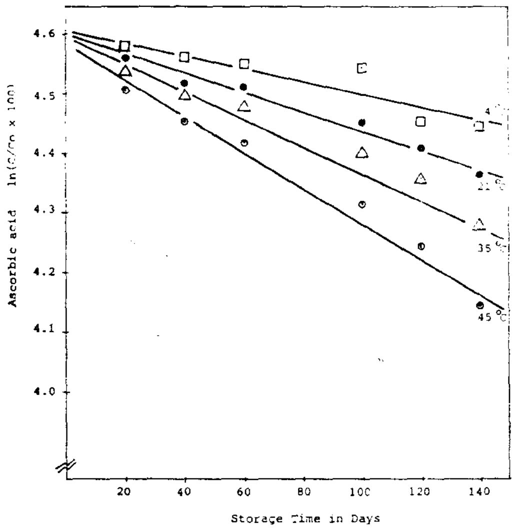

Fig. 1. First-order plots for degration of Ascorbic acid in powdered beverage
C: Ascorbic acid conc. after storage
C_0: Intial ascorbic acd conc.

Results and Discussion

Order of ascorbic acid destruction

Plots of the logarithm of ascorbic acid concentration versus storage time resulte in straigt lines(Fig. 1), which indicated a first order reaction. The half-life calculated from the rate constant for ascorbic acid degradation at 35°C was 330 days, which was similar to that in tomato juice of 37.8°C report by Lee *et al.*[11]

Effect of storage temperature

The first order rate constants determined for the powdered beverage at various storage temperatures are presented in Table 3. The result indicated that the rate of ascorbic acid destruction increased with increasing storage temperture. The Arrhenius equation is often used to account for temperature dependence of the reaction rate. Based on the rate constants summarized in Table 3, an Arrhenius plot was prepared (Fig. 2). An activation energy (*Ea*) for destruction of ascorbic acid in the powdered beverage was calculated as 3.32 Kcal/mole.

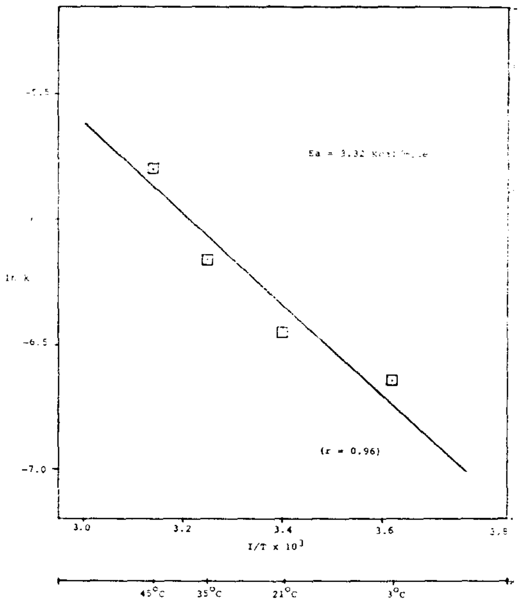

Fig. 2. Arrhenius plot of ascorbic acid destruction in powdered beverage

Blaug and Hajratwala[12] reported an Ea for the aerobic oxidation of ascorbic acid in a buffer system as 10.9 Kcal/mole and the Ea for anaerobic destruction of ascorbic acid was calulated as 3.3 Kcal/mole by Lee *et al.*[11] The data showed that the Ea for destruction of ascorbic acid in powdered beverage was close to Ea for anaerobic destruction of ascorbic acid.

Relationship between ascorbic acid and quality of powdered beverage

At each storage conditions, subjective evaluation for flavor and objective determination for ascorbic caid concentration were made at 20-day intervals for 6 months. The results of sensory evaluations are shown in Table 4.

The results indicated that the flavor score of the stored beverage decreased with increase in storage time. andthis was more obvious at higher storage temperatlture, was found that samples with flavor score less than 3 had an objectionable flavor. The relationship between sensory score and retention of

Table 4. Flavor score of powdered beverage during storage at various temperatures

Storage time(day)	Storage temp. (°C) 21°	35°	45°
0	7.67*	—	—
20	7.35	5.79	5.45
40	6.40	6.27	4.98
60	7.00	7.00	5.50
100	6.98	6.91	4.87
120	6.40	4.90	4.01
140	6.10	5.88	3.71
180	5.60	3.96	2.67

* Each value was a mean sensory score of 15 trained panelists

Flavor scores were based on the hedonic scale;

1 = extremely dislike
3 = moderately dislike
5 = niether like nor dislike
7 = moderately like
9 = extremely like

ascorbic acid is shown in figure 3. The linear regression equation for this relationship was;

$Y = 4.89X + 58.99$ $(r = 0.79)$

where, Y = flavor score

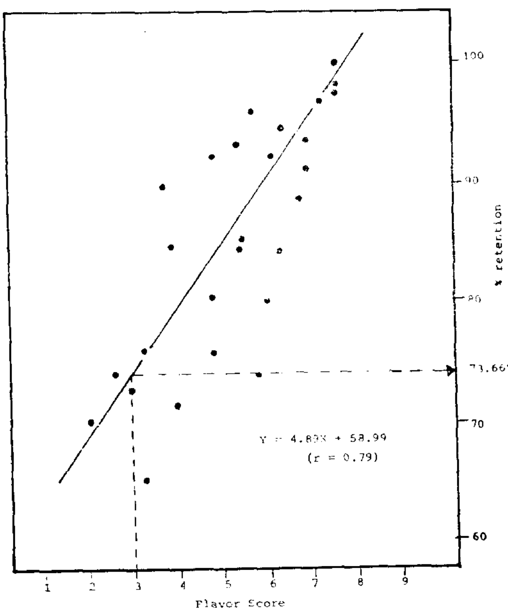

Fig. 3. Relationship between ascorbic acid and flavor score for powdered beverage

X = retention of ascorbic acid

It could be estimated from Figure 3 that beverage samples with ascorbic acid destruction over 25% would have an objectionable flavor.

Mathematical prediction model

In this study, temperature and time were considered as main factors which affected destruction of ascorbic acid in the powdered beverage. A mathematical prediction model was developed based on the following informations;

(1) The destruction of ascorbic acid followed a first order reaction

$$\ln C_t/C_0 = -Kt \quad \cdots\cdots(1)$$

where, C_0; initial concentration of ascorbic acid

C_t; concentration of ascorbic acid at the selected storage time, t.

Equation (1) could be modified for calculation of % retention of ascorbic acid at time, t.

$$\% \text{ retention} = e^{-Kt} \times 100 \quad \cdots\cdots(2)$$

(2) The effect of temperature on the reaction rate constant could be accounted for by the Arrhenius equation.

$$\ln K = \ln A - \frac{Ea}{RT}$$

$$\text{or } \log \frac{K_2}{K_1} = \frac{Ea}{2.303R}\left(\frac{T_2 - T_1}{T_2 T_1}\right) \quad \cdots\cdots(3)$$

where. K_1 = rate constant at temperature T_1

K_2 = rate constant at temperature T_2

R = gas constant (1.987 cal/mole °K)

A = pre-exponential constant

Ea = activation energy for destruction of ascorbic acid (cal/mole)

(3) The fluctuation of temperature during storage could be simulated by the Fourier series[11],

$$f(X) = \frac{a_0}{2} + \sum_{n=1}^{\infty}\left(a_n \cos\frac{n\pi X}{L} + b_n \sin\frac{n\pi X}{L}\right) \cdots(4)$$

where, L = limit of cycle

X = time in dadys

$f(X)$ = storage temperature as a function of storage time

An attempt was made to evaluate whether the Fourier series could simulate seasonal temperature fluctuation. Average temperatures of 10 years in Seoul area were used as input data, and a comparison of temperature simulated by the Fourier series with the

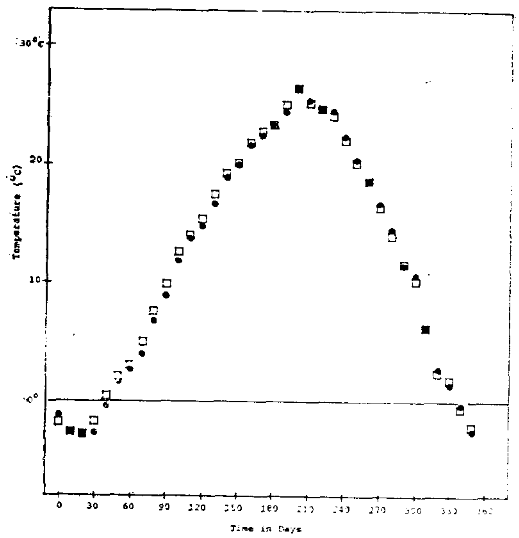

Fig. 4. Simulation of seasonal temperature changes by using the Fourier Series

● Temperature claculated by the Fourier Series

□ Reperted daily temperature in Seoul area (monthly weather report)

actual temperature in Seoul area are shown in Figure 4. The result in Figure 4 showed that the simulated temperature was very close to the actual input temperature.

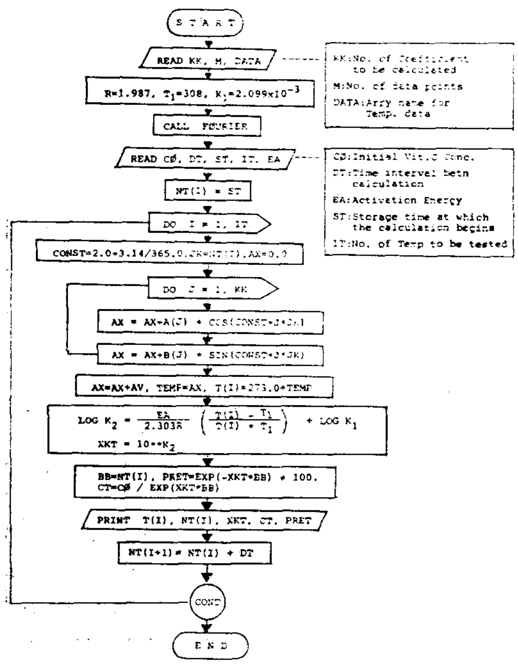

Fig. 5. Flow chart of the prediction model

A flowchart to calculate the retention of ascorbic acid in the powdered beverage as function of storage temperature and time is shown in Figure 5 and 6. The computer program required an initial concentration of ascorbic acid in the beverage, an activation energy for destruction of ascorbic acid and temperature profile during storage. The program, then, calculated and printed out the storage time, storage temperature, the reaction rate constant and % retention of acorbic acid.

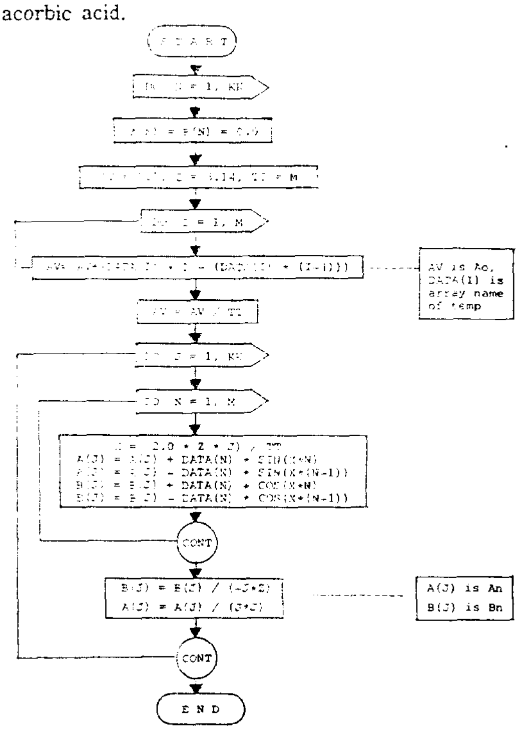

Fig. 6. Flowchart of subroutine fourier

Prediction of ascorbic acid stability

Since the simulation program could predict ascorbic acid stability as a function of temperature and time, the suitable storage condition of powdered beverage for the desired quality could be selected by using this program. The ascorbic acid stability in powdered beverage predicted by the simulation program is shown in Figure 7. In Figure 7, the results obtained from shelf-life tests were compared with the predicted results. The difference between the determined results and the predicted values was in a range of 0~3% retention with a mean difference of $0.34 \pm 1.18\%$ retention.

The good agreement between the predicted and the determined results indicated that the model could predict the ascorbic acid stabilty in the powdered beverage with reasonable accuracy. The mathematical prediction model performed its function well within the boundary of the system, indicating its possible application to dehydrated food product.

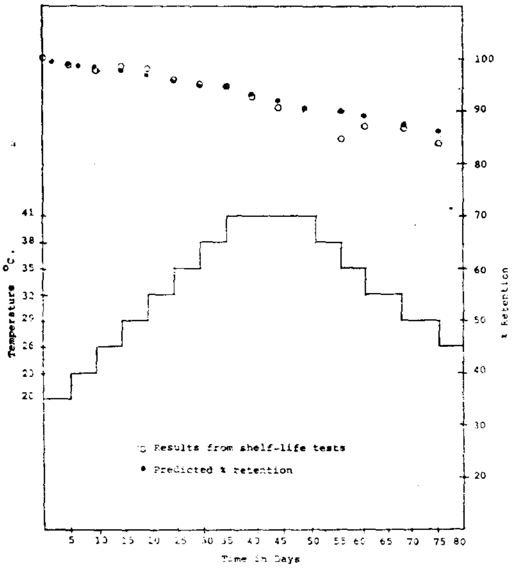

Fig. 7. Ascorbic acid stability with temperature fluctuation as a step function

요 약

오렌지향을 갖는 분말음료의 모델시스템을 설정하여 각기 4°, 21°, 35°, 45°,C에서 약 180일간 저장하여 아스코르빈산의 파괴를 측정하였다. 본 모델시스템에서 아스코르빈산의 파괴는 1차 반응이었으며 반응속도에 대한 온도와의 관계는 Arrhenius식에 따랐다. 아스코르빈산의 파괴에 대한 활성화 에너지는 3.3 Kcal/mole 이었으며 아스코르빈산의 잔존량과 향미 평점간의 상관관계에서 25% 이상 파괴되면 이미를 느낄 수 있었다. Simulation 모델을 적용하여 분말음료의 품질을 예견한바, 저장시험의 결과와 Simulation간의 오차는 약 3%이내로 매우 만족스러웠다. 이러한 결과로 분말음료의 품질을 Simulation을 이용하여 예견할 수 있음을 보여주었다.

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