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STUDY TOWARDS THE DEGRADATION KINETICS OF VITAMIN C BY REDOX TITRIMETRY IN FRESH POMEGRANATE JUICES OF ARAKTA CULTIVARS

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Abstract

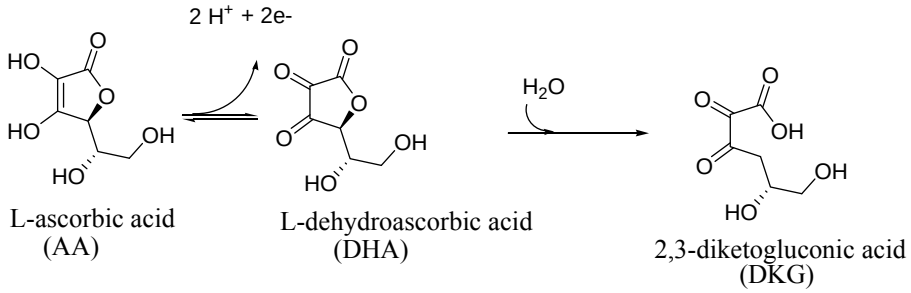
The aim of present investigation is to assess the effect of storage temperature and sugar addition on the composition of vitamin C in fresh pomegranate juices of Arakta variety and its degradation kinetics byredox titrimetry. The study revealed that, the degradation reaction of vitamin C follows zero-order kinetics in all types of juices. The degradation reaction rate constants obtained for juices K, L, M and N were 4.41; 3.61; 2.31and 1.84 mg vitamin C(per100 ml/ h) respectively. The activation energy for the degradation reaction of vitamin C in fresh juices with sugar addition was found higher compared to those prepared without sugar addition.

Keywords: Vitamin C, Pomegranate juice, degradation reaction, activation energy.

1. Introduction

In recent years, there is an increasing demand for nutritious food for healthy and better life of human beings hence efforts are made in this direction to exploit the nutrient retention in processed as well as stored food and allied products. Pomegranate (*Punicagranatum* L.) is a non-climatic multi seeded berry which is included under medicinal plants since early time and usually used as folk medicine in the India as medicament for antiviral, antifungal, antimicrobial and antibacterial agent [1].Vitamin C plays crucialrole for the inhibition of scurvy, maintenance of glowing skin, gums and blood vessels. Moreover it reduces the risk of obstructive pulmonary, cardiovascular diseases and non-hormone tumours [2].A daily intake of about 10-15 mg/day is generally required for adults to avoid deficiency and stave off scurvy. As L-ascorbic acid (AA) is a water-soluble, thermally sensitive vitamin which is predominantlyliable to chemical and enzymatic oxidation, its concentration can be considered as a quality factor in fruit juices and is therefore essential to monitor during processing and storage [3]. In the oxygen atmosphere, L-ascorbic acid (AA)get readily oxidized via a reversible reaction to L-dehydroascorbic acid (DHA), which possesses a similar biological activity as AA [4].This mild oxidation reaction reduces an antioxidant

activity five times lower than AA [5].The biological activity of vitamin C is lost when DHA is further despoiled by several ingredients, such as the hydrolysis with water to 2, 3-diketogulonic acid (DKG) [6].The structures of oxidation products including L-ascorbic acidare depicted in **Scheme1**.



Scheme 1: Aerobic oxidation of L-ascorbic acidand its oxidation products

Due to this phenomenon of aerobic oxidation, the quantitative estimation of vitamin C is specifically important in the production of soft drinks, pulps and fruit juices[7]. In addition, ascorbic acid is water soluble vitamin thereby causing substantial loss by boiling and then discarding the cooking water [8].The degradation of ascorbic acid upon storage is the main problem of nutritional quality loss in pomegranate juices which also determine their shelf life. This element is important to the juice manufacturers for proper process and storage of the juice under appropriate conditions. Consequently there is need tounderst and the ascorbic acid degradation reaction by investigating its kinetics in fresh pomegranate juices during storage.

In literature there are limited reports which describe the different kinetic studies models to estimate the rate constants for the degradation of vitamin C in various fruit juices. Few of the mused zero-order [9], first order [10], pseudo-first order [11] and second order kinetic reactions [12]. However, there are only scarce studies on kinetics of ascorbic acid loss in pomegranate juices during storage. Herein we report our studies on the kinetics of degradation of vitamin C in freshly home-made pomegranate juices of Arakta varietyat a room temperature and at a refrigerated temperature for fixed time interval. Moreover the effect of sugar addition on the vitamin C loss in different pomegranate juices was also investigated. We employed directiodometry to evaluate the vitamin C content which is simple, reliable and cost effective method in terms of the instrumentation and reagents.

2. EXPERIMENTAL SECTION

2.1 Reagents

Ascorbic acid, vitamin C tablet, 0.1NKIO_3,0.1N$Na_2S_2O_3$,10%KI,0.01NI_2, 2N H_2SO_4, 1% Starch solution and Distilled water.

2.2 Fruit materials

Pomegranate fruits of Araktacultivars were collected from the pomegranate orchards situated nearby Lonand and adjoining area of Khandalatehsil of Satara district. The fruits of uniform size and nearly same colour and maturity were selected by visual observation and used for the experiment.

2.3 Juice preparation

Clean pomegranate arils of about 200 g were separated from pomegranate by hand picking and they are blended in a domestic mixer (Bajaj Mixer Grinder, GM- 550). The resulting pulp was filtered through muslin cloth to separate the white seeds and residues from the liquid concentrates. The liquid concentrates were then diluted by the addition of mineral water (1:3v/v) in order to obtain fresh pomegranate juice. Four types of fresh pomegranate juices were prepared, namely K, L, M and N. Juices K and M were stored at a room temperature of 28°C, whereas samples L and N were stored at a refrigerated temperature of 8°C. Similarly, juices L and N were prepared without sugar addition, while 5% sugar was added to juices M and N. No any preservatives were added and no thermal treatment was given to the juices. All of them were stored in closed glass stopper bottles.

2.4Determination of Vitamin C

Analysis of vitamin C in the juices was done on the same day of preparation of juices using direct iodometric titration. An aliquot of 25 $cm^3$of a fresh pomegranate juice was taken in a 250 cm^3conical flask followed by addition of 2cm^3 1% starch indicator. The resultant solution was titrated with 0.01 N iodine solutions which were previously standardized with sodium thiosulphate in the matrix of potassium iodide. At the end point a slight excess of iodine is added to the solution when colour changes from dark blue to black. Stoichiometric relationship for calculating the mg of ascorbic acid is 1cm^3 of 0.01 N iodine is equivalent to 0.8806 mg ascorbic acid[13].

The iodine is reduced by the ascorbic acid to form iodide as perredox equation (Eq.1).

$$I_2 + 2e^- \longrightarrow 2I^- \quad (1)$$

2.5 Data Analysis

Vitamin C in the fresh pomegranate juices were determined for the first 8 hours of storage exactly after the preparation with a time interval of 1 hr, considering the fact that the juices especially stored at 28°C were not acceptableorganoleptically any longer upon the storage beyond 8 hrs. The degradation of ascorbic acid in pomegranate juices upon storage would be estimated using zero-order (Eq.2) and first-order kinetic models (Eq.3). The most appropriate model was selected based on the correlation coefficients(R^2) calculated using the least square procedure.

$$C = C_0 - k_0 t \quad (2)$$

$$C = C_0.\exp(- k_1 t) \quad (3)$$

Where C is the ascorbic acid (AA) concentration (mg AA/100 cm^3 juice) at time t,

C_0 the ascorbic acid concentration attime 0,

k_0 and k_1 the ascorbic acid degradation rate constant for the zero order (mg AA/(100 cm^3 juice. hr)) and for the first order (h^{-1}), respectively,

t the storage time (hr).

Half-life time ($t_{1/2}$) 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_0). Half-life of each pomegranate juice at its corresponding temperature storage is determined using the kinetic models (Eq.2 or Eq.3) depending on the best fitted model to the experimental data. Arrhenius equation (Eq.4) was employed in order to check the temperature dependence of the ascorbic acid degradation in terms of the activation energy (Ea).

$$k_A = k_B.\exp\left[-\frac{Ea}{R}\left(\frac{1}{T_A} - \frac{1}{T_B}\right)\right] \quad (4)$$

Where k_A and k_B are ascorbic acid loss at storage temperatures T_A (28°C) and T_B (8°C),

Ea is the activation energy for the ascorbic acid degradation(kcal/ mol), R is the universal gas constant (1.987 cal/ mol.) and T is the absolute temperature.

3. RESULTS AND DISCUSSION

3.1Modelling degradation kinetics of pomegranate juices

All experiments were conducted in replicate and results were reported as average. General linear and nonlinear fitting procedures for analysis were determined using ORIGIN software version 6.0.

The degradation of vitamin C in fresh pomegranate juices was studied in terms of ascorbic acid (AA) concentration. The degradation of ascorbic acid in pomegranate juices fitted by zero-order and first-order kinetics models as depicted in Fig.1

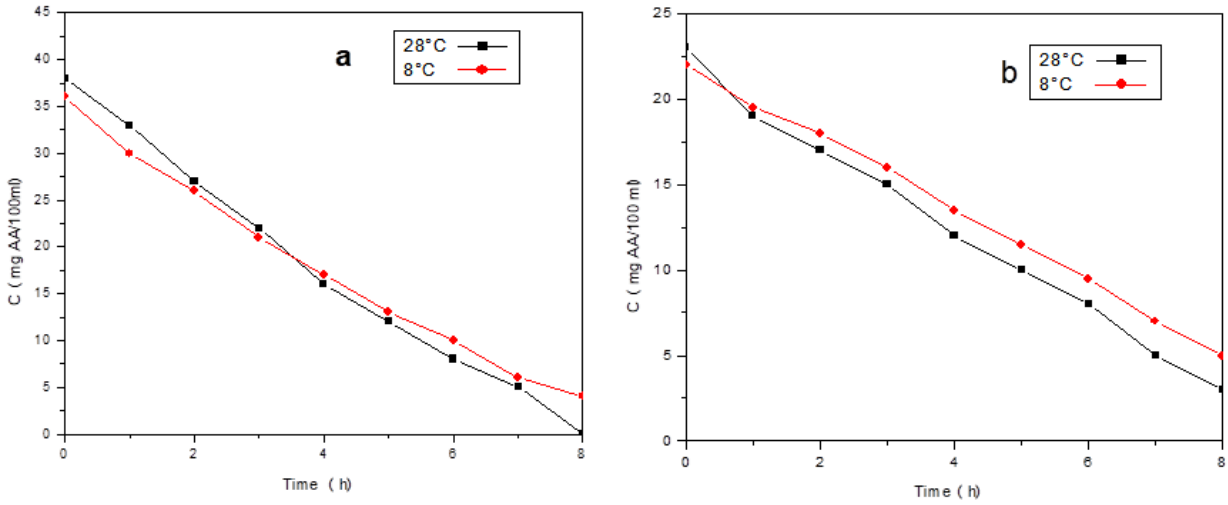


Fig.1 Ascorbic acid degradation during storage at 28°C (■)and 8°C (●)of fresh pomegranate juices prepared (a) without sugar (b) with sugar.

It has been found that the degradation of ascorbic acid in all fresh pomegranate 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 K*vs.* juice L and juice M*vs*. juice N). In contrast, the rate constants were decreased almost in half upon sugar addition into the juices (juice K*vs.* juice L and juice M*vs.* juice N). The deterioration rate of vitamin C was been found to be maximum in juice K and the lowest in juice N (Table 1). 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. 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 as described by Van Bree*et al.* [9]. It is likely that in these freshly made pomegranate juices, the rapid vitamin C degradation might occur during the first one hour

following first order kinetic model, followed by slower degradation rate according to zero order kinetic reaction model.

Table 1 displays the kinetic parameters such as ascorbic acid loss rates their R^2 correlations obtained from the fitting using Equation 2 and 3as kinetic models.

Table 1Kinetic loss rates constants and R^2 values according to zero-order and first order kinetic models in fresh pomegranate juices

Pomegranate juice	Storage temperature (°C)	Sugar	Zero order			First order	
			k_o (mg AA/100cm^3.h)	R^2	$t_{1/2}$ (h)	k_1 (h^{-1})	R^2
K	28°A	Without sugar	4.418	0.996	4.180	0.390	0.809
L	8°C	Without sugar	3.613	0.994	4.782	0.224	0.965
M	28°C	With sugar	2.319	0.995	4.646	0.238	0.943
N	8°C	With sugar	1.845	0.995	5.597	0.146	0.959

The juices particularly stored at 28°C were deteriorated and organoleptically unaccepted beyond 8 hr of storage time probably due to the microbial activity. Juice Npossesses the longest half-life of about 5.597hrs.compared to juice K whose half time is about 4.180hrs. (Table1). All these evidences reveal a synergetic effect between low temperature storage and the presence of sugar which effectively inhibit the degradation of vitamin C in fresh pomegranate juices. The activation energy of ascorbic acid degradation estimated for the fresh pomegranate juices prepared without and with sugar were 1.63 kcal/ mol and 1.89kcal/ mol, respectively. These values were compared with the *Ea* for ascorbic acid loss in red fruit as studied by Verbeyst*et al*.[14]. Higher activation energy of the fresh pomegranate 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. The reasonably low activation energy and short half life time of ascorbic acids obtained demonstrates the proneness of vitamin C in freshly home-made pomegranate juices to a rapid degradation process.

3.2 Effect of Sugar addition on vitamin C loss in pomegranate juices

It has been reported that sucrose was able to inhibit ascorbic acid oxidation in a closed aqueous system[15].We compared the loss of vitamin C content in the juices as a function of time which were stored at two different temperatures with and without sugar addition. The corresponding results are depicted in Fig.2.

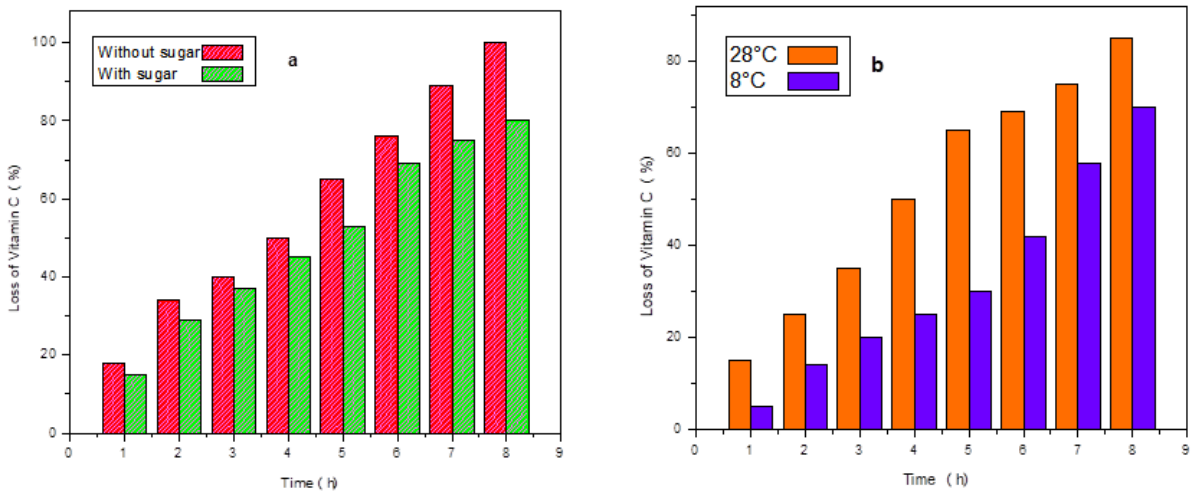


Fig.2 Comparison of vitamin C loss in fresh pomegranate juices stored at 28°C and 8°
(a) without sugar (b) with sugar.

From Fig.2 it has been observed that, the ascorbic acid loss was decreased when the juice was stored at the refrigerated temperature. The ascorbic acid loss in juice after 8hour storage time were found to be completely degraded(100%) in the juice stored at room temperature and without sugaraddition. Whereas in the juice stored at refrigerated temperature and with sugar addition the ascorbic acid loss could be suppressed to about 70% (Fig.2a). Furthermore, the ascorbic acid loss was decreased upon sugar addition (Fig.2b), this suggests that the degradation rate of vitamin C in the fresh pomegranate juices may be retarded simply by the addition of sugar as a common sweetening ingredient in fruit juices. More interestingly, storing the fresh pomegranate juices at low temperature combined with sugar addition could significantly suppress the ascorbic acid loss (Fig.2b). After 8 hours, the ascorbic acid loss in juice K reached almost to 100%compared to juice N where only 70% loss was noticed.

4. CONCLUSIONS

We have elucidated the degradation kinetics of vitamin C in pomegranate juices at two temperatures and its dependence on time and sweetening agent. The Vitamin C concentration in all pomegranate juices was decreased with storage time and the degradation of vitamin C of all 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 cm^3. h), respectively. The activation energy calculated for the vitamin C degradation in fresh pomegranate juices with sugar and without sugar addition were 1.89 kcal/ mol and 1.63 kcal/ mol respectively. The ascorbic acid degradation after 8hour storage time were found 100% in the juice stored at room temperature and without sugar addition, while it is suppressed to about 70%in the juice stored at refrigerated temperature and with sugar addition.

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