Vitamin C degradation during storage of fortified foods

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Summary

The papers on the degradation of vitamin C in fortified foods have been reviewed. In order to compare the data published, the rate constants of degradation have been calculated assuming the first-order kinetics of degradation. It has been shown that temperature, the form of vitamin and the matrix are the factors affecting most the stability of vitamin C in foods and beverages. Lower storage temperature brings about a higher retention of vitamin C. The matrix also affects the rate constants of degradation. For liquid matrices and for comparable temperatures, the rate constants are much higher for the degradation in milk that in fruit juices and drinks. As for the solid matrices, the rate constants of vitamin C degradation in bread are by 2–3 orders of magnitude higher than those for the bran flakes, cereals, dried apple chips and potato flakes. The literature data indicate that encapsulation is the best way of protecting vitamin C.

Keywords

vitamin C; fortification; storage; temperature; rate constant

Vitamin C attracts attention of the research community and consumers as a nutrient with a broad biological activity and importance for human health. It is a white, crystalline, odourless, water-soluble compound. Main sources of vitamin C are fruits and vegetables (green and red peppers, collard greens, broccoli, spinach, tomatoes, potatoes, strawberries, oranges, etc.). Vitamin C supports the absorption of iron and the formation of collagen. Vitamin C is often added to foods not only as a nutrient (to make up for processing losses) and an antioxidant [1], but it is added also in order to prevent the browning of fresh and canned fruits and vegetables, the acidification of meat and avoid the haze formation in brewed products (such as beer) [2]. Vitamin C is often added as a fortificant to fruit juices, fruit-flavoured drinks, juice-added soda waters, dry cocktails or beverages, cereal-based products, and milk. General principles for the addition of essential nutrients to foods are given by the Codex Alimentarius Commission. The Codex definition of fortification is „the addition of one or more essential nutrients to a food whether or not it is normally contained in the food, for the purpose of preventing or correcting a demonstrated deficiency of one or more nutrients in the population or specific population groups“ [3].

Vitamin C is an antioxidant and, in water, it readily oxidizes first to dehydroascorbic acid, then to diketogulonic, oxalic, and threonic acids. The first reaction is reversible, but the subsequent ones are not. Hence, its content in food can decrease during food preparation and storage. Ascorbic acid is recognized to be one of the most heat sensitive nutrients in foods, therefore, it is a marker of the loss of other nutrients [4]. The aim of this article is to review the papers on ascorbic acid degradation in fortified foods at various storage temperatures. For the sake of comparing the published data and finding relevant trends, the rate constants of degradation are calculated.

REVIEW OF VITAMIN C LOSSES

Storage of fortified beverages

The decrease of vitamin C content with time has been recently studied in a number of papers. MURTAZA et al. [5] studied the content of ascorbic acid in a strawberry drink which was stored at room temperature (25 °C), refrigeration temperature (4–6 °C) and high temperature (40–45 °C). Minimal changes were observed in the samples stored in a refrigerator. Decrease was from 65.0 mg/100 ml

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Tab. 1. Degradation rate constants of vitamin C changes during storage in some beverages.

Beverages	Storage conditions	Time [h]	Retention [%]	Degradation rate constant $10^4\,k_0$ [h^{-1}]	References
strawberry drink	4–6 °C	2160	67.7	18	MURTAZA et al. [5]
yellow passion fruit juice	37 °C	336	0	270	TALCOT et al. [7]
blood orange juice	4.5 °C	1176	25.1	12	CHOI et al. [8]
powder fruit drinks	21 °C	24	84	73	MEHANSHO et al. [11]
Cola beverages	15 °C AA	600	83.1	3.1	WANG et al. [10]
	15 °C AMP		97.7	0.39	
	15 °C APP		97.7	0.39	
	25 °C AA		70	6.0	
	25 °C AMP		90	1.8	
	25 °C APP		95.4	0.78	
	35 °C AA		63.8	7.5	
	35 °C AMP		68.4	6.3	
	35 °C APP		93.8	1.1	
dry fruit drink mix	23 °C	8760	94	0.071	DE RITTER [12]
apple juice			68	0.44	
cranberry juice			81	0.24	
grapefruit juice			81	0.24	
pineapple juice			78	0.28	
tomato juice			80	0.25	
vegetable juice			68	0.44	
grape drink			76	0.31	
orange drink			80	0.25	
carbonated beverages			60	0.58	

AA - L-ascorbic acid, AMP - L-ascorbate 2-monophosphate, APP - L-ascorbate 2-polyphosphate.

to 44 mg/100 ml after three months. The loss of flavour and taste might be due to the degradation of ascorbic acid [6].

TALCOTT et al. [7] fortified the yellow passion fruit juice with ascorbic acid and sucrose. The juices were stored for 28 days at 37 °C. After 14 days of storage, ascorbic acid was completely degraded and browning effect of juice was observed. It was concluded that ascorbic acid and sucrose fortification exhibited preservation effect on carotenoids. CHOI et al. [8] studied retention of ascorbic acid and pigment stability in blood orange juice. Fortified and controlled samples of juices were stored for 7 weeks at 4.5 °C. In fortified juices, a greater retention at the level of 25.1% of ascorbic acid was observed. Experiments with orange juices packed in Tetra Brik Aseptic cartons showed that retention of L-ascorbic acid is greatly affected by the storage temperature (4–50 °C). This fortification led to an increase of the shelf life of orange juices [9].

WANG *et al.* [10] studied the stability of carbonated beverages fortified with L-ascorbic acid, L-ascorbate 2-monophosphate and L-ascorbate 2-polyphosphate. Beverages were stored in dark, at 15 °C, 25 °C and 35 °C during 6 weeks. L-ascorbate 2-monophosphate was the most stable form of vitamin C during storage at 25–35 °C.

MEHANSHO et al. [11] studied the stability of vitamins and minerals in powder fruit drinks. The drinks contained three minerals (iron, zinc and iodine) and eight vitamins (vitamin A, E, C, B_6, B_2, B_{12}, niacin and folic acid). Fortified powder fruit drinks were stored in a thermostatted room at 21 °C for 1 year. All nutrients were stable after 12 months storage. Stability of vitamin C from reconstituted fortified powder fruit drinks was followed during 24 hours. After 1 hour, 94% of vitamin C was retained, and after 24 hours 84% of vitamin C was retained.

DE RITTER [12] observed that the retention of vitamin C in various fortified foods and beverages stored for 12 months at 23 °C ranges was from

60 to 97%. The highest retention of vitamin C was in solid foods (cocoa powder) and the lowest one in beverages (carbonated beverages). The corresponding values are listed in Tables 1–3.

Storage of fortified milks

Since the milk is low in iron and vitamin C content, it is desirable to fortify milk with them [13, 14]. Löker et al. [13] improved the composition of milk with vitamin C, iron and zinc. Milk was fortified with 50, 45, 40, and 30 mg/100 g of vitamin C and stored for 7 days in a refrigerator. The experiments demonstrate that the addition of vitamin C in the amount of 30 mg/100 g was appropriate, because the acidity of milk did not increase noticeably and no negative effect on sensory quality was observed. Rosenthal [14] studied the degradation in the milk fortified with ascorbic acid (100 mg/100 ml) and iron (5 mg/100 ml). No differences were reported in oxidation levels in fortified milk (thiobarbituric acid reactive substances TBARS value = 0.61 $mg.kg^{-1}$) and unfortified milk (TBARS value = 0.71 $mg.kg^{-1}$) over 7 days storage at 4 °C in the dark. Losses of ascorbic acid from pasteurized milk, with and without added ferrous lactate, were 35–40 %. Lee *et al*. [15] evaluated the efficiency of L-ascorbic acid microencapsulated by polyglycerol monostearate in milk during 12 days of storage at 4 °C. After 5 days the release of L-ascorbic acid from the microcapsules was 6.6% and after 12 days 9.2%. The results indicated that microencapsulation of L-ascorbic acid by polyglycerol monostearate can be applied for milk fortification. Sharma [16] studied the stability of milk with microencapsulated vitamin C. Average total vitamin C content in unfortified raw, pasteurized (63 °C for 30 min) and sterilized (121 °C for 15 min) buffalo milk were 23.47, 20.09 and 11.34 $mg.l^{-1}$, while in milk samples fortified with encapsulated ascorbic acid were 366.71, 345.80 and 210.74 $mg.l^{-1}$, and for milk samples fortified with non-encapsulated ascorbic acid were 364.84, 322.37 and 203.21 $mg.l^{-1}$, respectively. The instability of vitamin C raises the question of impact of the process and storage on the fortified milks. Gliquem and Birloouez-Argon [17] demonstrated that the vitamin C added to fortified milks undergoes degradation during storage depending on the type of heat treatment and permeability of the packaging material to oxygen. The effect of sterilization method (ultra-high temperature at 135 °C, 4 s and sterilization in bottle at 110 °C, 20 min) was apparent only during the first days of storage. Decrease in vitamin C content after 3 days storage at room temperature represent 35% of the initial value, after 1 month in a 3-layered packaging material 99%, in a 6-layered packaging 51%, and after 4 months in the 6-layered packaging material 75% of the vitamin C degraded.

Storage of solid foods

Park *et al*. [18] studied the stability of several forms of vitamin C during production and storage of white pan bread. The bread contained large, middle-sized and small crystals of ascorbic acid coated with fat. The bread fortified with large crystals of ascorbic acid exhibited a higher retention of ascorbic acid by 20% than the bread fortified with small crystals of ascorbic acid or with uncoated ascorbic acid. After 3 days of storage the bread fortified with L-ascorbate 2-polyphosphate and L-ascorbate 2-monophosphate retained by 10–15% more vitamin C than the bread fortified with non-phosphorylated ascorbic acid. Park et al. [19] investigated white bread fortified with fat-coated ascorbic acid (hydrogenated soybean oil). The bread placed in polyethylene bags and stored at 25 °C for 7 days showed 15% retention of ascorbic acid. When ascorbic acid was added to bread with β-carotene, the retention of β-carotene increased in proofed dough but this treatment failed to protect β-caro-

Tab. 2. Degradation rate constants of vitamin C changes during storage in milk.

Milks	Storage conditions	Time [h]	Retention [%]	Degradation rate constant $10^4\ k_0$ [h^{-1}]	References
fortified milk	25 °C, 3-layered packaging material	720	1	32	Gliquem and Birloouez-Argon [17]
	25 °C, 6-layered packaging material	720	49	10	
	25 °C, 6-layered packaging material	2880	25	5	
fortified milk	4 °C	120	90.6	3.5	Loker et al. [13]
evaporated milk	23 °C	8760	75	0.33	De Ritter [12]

Tab. 3. Degradation rate constants of vitamin C changes during storage in some solid foods.

Solid foods	Storage conditions	Time [h]	Retention [%]	Degradation rate constant 10^4 k_0 [h^{-1}]	References
bread	25°C, polyethylene bags	168	15	113	PARK et al. [19]
bread with fiber	25 °C, moisture 45%	168	3	208	PARK et al. [21]
bread without fiber	25 °C, moisture 37%	168	14	117	
bread with reduced iron and AMP	25 °C	144	52	45	WANG et al. [10]
bread with reduced iron and AA	25 °C	144	18	120	
bran flakes	25 °C, 7% moisture	720	95	0.71	WANG et al. [10]
	40 °C, 11% moisture	720	20	22	
ready-to-eat cereal	23 °C	8760	71	0.39	DE RITTER [12]
cocoa powder	23 °C	8760	97	0.035	
ready-to-eat cereals	room temperature	8640	60	0.58	STEELE [22]
cereals	40 °C	2160	93	0.34	ANDERSON et al. [23]
	22 °C	4320	94	0.14	
dried apple chips	7 °C, 45% relative humidity	6480	80.4	0.34	KONOPACKA and MARKOWSKI [26]
	18 °C, 90% relative humidity	6480	63.1	0.71	
potato flakes	25 °C AA	3096	18	5.5	WANG et al. [25]
	25 °C AMP		88	0.41	
	25 °C APP		84	0.56	

AA - L-ascorbic acid, AMP - L-ascorbate 2-monophosphate, APP - L-ascorbate 2-polyphosphate.

tene and ascorbic acid in the stored bread. After storage for 7 days ascorbic acid was completely destroyed.

In tested dough, before the bread production, retention of ascorbic acid was 99%. This high retention was attributed to the effect of yeast, which consumed oxygen during processing and so protected ascorbic acid from oxidation [20]. Bread fortificated with ascorbic acid, with or without fibre was stored for 7 days at 25 °C. The retention of antioxidant was 3% at 45% moisture in the fibre containing bread and 14% at 37% moisture in bread containing no added fibre. During storage, ascorbic acid disappeared faster in the case of bread with added fibre than in bread without added fibre. It was induced by the higher moisture content in the fibre bread [21]. WANG et al. [10] studied the ascorbic acid stability in bread. The bread was made with reduced iron and L-ascorbate 2-monophosphate addition. After 6 days of storage at 25 °C, 48% of vitamin C was lost. Bread made with reduced iron and L-ascorbic acid addition lost after the same long storage 82% of vitamin C amount. Ferrous iron in bread caused total destruction of L-ascorbic acid after 6 days storage at 25 °C. Stability of L-ascorbic acid in bread depended on the type of iron enrichment.

Vitamin C retention in cereal-based products appears to be dependent on time, temperature and product moisture. Storage time and baking decrease ascorbic acid content, however, encapsulation in soybean oil appears to reduce its losses. STEELE [22] investigated content of vitamin C in ready-to-eat cereals. General loss in vitamin C content during production of ready-to-eat cereals was approximately 37%. Stability of ascorbic acid in fortified cereals stored at room temperature was also determined over a 12 months period. Ascorbic acid was stable over the initial 4 months, after that time its amount decreased dramatically. After a 12 month period, its retention was 60%. Similarly, ANDERSON et al. [23] indicated that cereals stored for 3 months at 40 °C or for 6 months at 22 °C retained 93 and 94% of ascorbic acid, respectively.

WANG *et al.* [10] studied bran flakes fortified with varied forms vitamin C. Bran flakes were stored for 7 months at 25–40 °C moisture content was 7–11%. Loss of ascorbic acid was rapid, i.e. 80% after 1 month at a higher moisture (11%) and temperature (40 °C). 75% losses were at 9%

moisture and 40 °C, 50% at 7% moisture and 40 °C, and 5% at 7% moisture and 25 °C. During the first 2 months of storage compared to the last 5 month, the losses of ascorbic acid were much more rapid.

YEH et al. [24] followed peanut spread, fortified with vitamin A, B_6, C, thiamin, riboflavin, calcium, and iron. The spreads were stored for 3 months at various temperatures (4, 23 and 40 °C) in a dark place. Vitamin C and other water soluble vitamins were relatively stable in deaerated peanut spreads. Vitamin C was used as a nutrient and it was efficient as an antioxidant when dispersed in oil. The research showed that encapsulation of ascorbic acid in soybean oil reduced its losses.

Fortified mashed potatoes stored for 4.3 months at 25 °C were investigated by WANG *et al*. [25]. Three forms of vitamin C (L-ascorbic acid, L-ascorbate 2-polyphosphate and L-ascorbate 2-monophosphate) were added. The retention of L-ascorbic acid was 18%, L-ascorbate 2-polyphosphate 84% and L-ascorbate 2-monophosphate 88%. I was concluded that L-ascorbate 2-monophosphate was more stable in stored potatoes.

KONOPACKA and MARKOWSKI [26] reported ascorbic acid retention of 83% in dried apple chips during production. Ascorbic acid retention after 9 months of storage was 80.4% for favourable (7 °C, 45% relative humidity) and 63.1% for unfavourable conditions (18 °C, 90% relative humidity), respectively.

MARCHETTI *et al*. [27] compared the rates of vitamin C and other vitamins degradations when mixed with metal sulphates or metal amino acid chelates of copper, zinc, iron, manganese, and cobalt. The mixes were stored at either 20 or 37 °C and vitamin C content was measured after 90 and 180 days. Loss of ascorbic acid in the mixes was less when stored with metal amino-acid chelates than with metal sulphates, regardless of storage time.

The literature data indicate that encapsulation is the best way of protecting vitamin C. For the application in solid food systems (cereals, bread, and biscuits), spray-cooling, spray-chilling and fluidized bed [28] appear the best form of encapsulation. In liquid food systems, liposomes represent the best way [29].

Evaluation of the rate constants of vitamin C degradation

The authors use various modes of expressing the content of vitamin C. In order to compare quantitavely the published results, we calculated the rate constants of the degradation assuming the first-order kinetics. The results are given in Tables 1-3.

From the values of rate constants it is seen that temperature is probably the most important factor affecting the degradation. It is clearly seen for the cola beverages (Table 1), where the rate constant increases steeply with temperature [10]. In addition, from the values of the rate constants at various temperatures the activation energies can be calculated. For the cola beverages stabilized with ascorbic acid, the activation energy is 32.8 $kJ.mol^{-1}$, for those stabilized with L-ascorbate 2-monophosphate the activation energy is 102.8 $kJ.mol^{-1}$, and 38.4 $kJ.mol^{-1}$ for those stabilized with L-ascorbate 2-polyphosphate. The value of activation energy is a measure of sensitivity of the system towards degradation. The effect of temperature is pronounced also for cereals [23]. In this case, the activation energy of degradation is 37.9 $kJ.mol^{-1}$.

Various forms of vitamin C degrade with different rates. From the rate constants for cola beverages (Table 1), the order of rate constants is ascorbic acid > L-ascorbate 2-monophosphate > L-ascorbate 2-polyphosphate. Approximately the same order can be seen for the potato flakes (Table 3). Also, the bread fortified with large crystals of ascorbic acid exhibited a higher retention of ascorbic acid by 20% than the bread fortified with small crystals of ascorbic acid or with uncoated ascorbic acid [18].

The matrix also affects the rate constants of degradation. For liquid matrices and for comparable temperatures, the rate constants are much higher for the degradation in milk that in fruit juices and drinks (Tables 1 and 2). This could be caused by different pH in both matrices. It has been reported that the rate of degradation increases remarkably when pH > 5.7 [30]. As for the solid matrices, the rate constants of vitamin C degradation in bread are by 2–3 orders of magnitude higher than those for the bran flakes, cereals, dried apple chips and potato flakes (Table 3).

The data of Tables 1–3 indicate that some effect on the rate constant could have also the relative humidity and the quality of packaging. However, the number of values is insufficient to draw an unequivocal conclusion.

CONCLUSIONS

The papers on the degradation of vitamin C in fortified foods have been reviewed. In order to compare the data published, the rate constants of degradation have been calculated assuming the first-order kinetics of degradation. It has been shown that temperature, the form of vitamin and the matrix are the factors affecting most the stability of vitamin C in foods and beverages. Lower storage temperature brings about a higher retention of vitamin C. The matrix also affects the rate constants of degradation. For liquid matrices and for comparable temperatures, the rate constants are much higher for the degradation in milk that in fruit juices and drinks. As for the solid matrices, the rate constants of vitamin C degradation in bread are by 2–3 orders of magnitude higher than those for the bran flakes, cereals, dried apple chips and potato flakes.

The literature data indicate that encapsulation is the best way of protecting vitamin C. For the application in solid food systems (cereals, bread, and biscuits), spray-cooling, spray-chilling and fluidized bed appear the best ways of encapsulation. In liquid food systems, liposomes represent the best form of encapsulation.

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Received 10 April 2006; revised 17 May 2006; accepted 23 May 2006.