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Influence of System Composition on Ascorbic Acid Destruction at Processing Temperatures

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Abstract: The anaerobic L-ascorbic acid (AAs) destruction in glucose aqueous model systems (water activity, a_w, 0·94) of pH 3·5, 4·1 and 5·0 was studied. The AAs degraded as a function of time and temperature (70, 80 and 90°C) with a behaviour that, in general, could be described by first order kinetics except for AAs in the system containing L-lysine, in which the results adjusted to zero order. The increment of pH from 3·5 to 5·0 accelerated AAs destruction and browning reactions. The addition of tin(II) or lysine to the glucose medium, increased AAs loss and browning. No difference was observed in AAs degradation and colour intensity when sorbic or propionic acid were used as antimycotics, at pH 3·5. Packaging the glucose system of acid pH with an air chamber, produced a faster destruction of AAs and browning of the solution than the one observed for the same system in anaerobic condition. In aerobic condition, the presence of glucose produced a lesser degradation of AAs than the one observed in the system without humectants.

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INTRODUCTION

Fruit and vegetables are significant sources of dietary vitamin C. The principal biologically active form of this vitamin is L-ascorbic acid (AAs) but an oxidation product, L-dehydroascorbic acid (DHA) is also active (Villota and Kavel 1980; Levine and Movita 1985). Its activity is commonly determined by the dye-titration method using 2,6-dichlorophenolindophenol (AOAC 1990).

Thermal treatments like blanching and pasteurization as well as evaporation are commonly applied during fruit juice processing producing degradation of vitamin C and non-enzymic browning (Massaioli and Haddad 1981; Leistner 1995).

Prediction of shelf-life of food products stored under different environmental conditions is a complex problem for food industry, because shelf-life depends on a large number of factors such as temperature, equilibrium relative humidity, oxygen partial pressure, light, package permeability and package configuration (Quast and Karel 1972; Bissett and Berry 1975; Mohr 1980; Massaioli and Haddad 1981). In particular with the advent of nutritional labelling regulations there has been considerable interest in the degradation rates of nutrients such as vitamin C in citrus juice. AAs undergoes aerobic destruction (oxidation) catalysed by cupric, silver, ferrous and stannous ions (Bissett and Berry 1975). Anaerobic degradation proceeds simultaneously but more slowly than aerobic one or is the unique path in absence of oxygen (Kurata and Sakurai 1967a). Non-enzymic browning (NEB) is considered one of the major causes of quality loss in citrus juices during storage, having an important role in flavour, colour and nutritional quality and is related to vitamin C loss (Lee and Nagy 1988).

According to prementioned facts, the purpose of this research work is to obtain information about ascorbic

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acid degradation, at high temperatures similar to processing ones, in sweet aqueous model systems (a_w 0·94) of acid pH (pH 3·5), trying to understand the influence of food components, oxygen presence and processing conditions on that degradation as well as the relation between that destruction and NEB.

MATERIALS AND METHODS

Systems composition is described in Table 1.

All reagents used were of analytical grade (Merck Química Argentina).

All systems contained water and D-glucose. Tin(II) or L-lysine were added to test their effect on AAs depletion. In general, sorbic acid was used as a preservative but system E contained propionic acid to evaluate its influence. The pH was adjusted with citric acid solution (50%, w/v) to a value of 3·5, 4·1 or 5·0 with the exception of system D in which phosphoric acid was used to adjust pH to 3·5. Water activity was adjusted to 0·94 through D-glucose addition. We also used a system without humectants as a control (system H). The pH measurement was performed with a combined glass electrode connected to a pH meter (Metrohm, pH meter E 632, Switzerland). Water activity was measured with a Novasina hygrometer (model Thermoconstanter Humidat THL/TH 1, Novasina, Switzerland) according to Kitic *et al* (1986).

In general, 60 ml glass flasks were completely filled with aliquots of each system excluding any headspace. The flasks were hermetically sealed to prevent evaporation and were stored in the dark, in constant temperature chambers regulated at 70, 80 and 90°C (±0·5°C). Storage was performed in duplicate for each system and condition. To study the effect produced by headspace, sixty millilitres of the systems of pH 3·5 with glucose (I) and without humectant (J) were bottled into 250 ml glass flasks, and stored as previously explained. At prefixed time intervals, samples were taken out and analysed as stated in the following paragraphs.

Absorbance measurement at 420 nm was performed with an Spectronic 21 spectrophotometer (Bausch and Lomb USA).

Vitamin C was determined with 2,6-dichlorophenol indophenol combined with xylene extraction (Rojas and Gerschenson 1991).

Dissolved oxygen was evaluated with an oxygen electrode (model 97-08-00, Orion Research Incorporated, Cambridge, MA, USA).

All measurements were performed in duplicate.

Rate constants (k) for AAs destruction or NEB were calculated through linear regression analysis of data and compared by analysis of covariance (ANACOVA) (Sokal and Rohlf 1969; Garrido and Sarchi 1990).

RESULTS AND DISCUSSION

The effect of time and temperature on AAs degradation for the different systems is described in Table 2.

For systems stored without headspace, after approximately 15–20 h the dissolved oxygen decayed to values ≃0·2–0·8 ppm, equivalent to zero if analytical error is considered (Rojas and Gerschenson 1991). As a conse-

TABLE 1
Chemical composition of model systems[a]

System	*pH*	*Composition*[b] (*g kg*$^{-1}$)						
		Glu	*KS*	*AAs*	*ProA*	*Tin(II)*	*Lys*	*W*
A	3·5	360	1·0	0·35	—	—	—	**[d]
B	4·1	360	1·0	0·35	—	—	—	**
C	5·0	360	1·0	0·35	—	—	—	**
D[c]	3·5	360	1·0	0·35	—	—	—	**
E	3·5	360	—	0·35	1·0	—	—	**
F	3·5	360	1·0	0·35	—	0·010	—	**
G	3·5	360	1·0	0·35	—	—	17·2	**
H	3·5	—	1·0	0·35	—	—	—	**
I[e]	3·5	360	1·0	0·35	—	—	—	**
J[e]	3·5	—	1·0	0·35	—	—	—	**

[a] All systems have a water activity (a_w) of 0·94, except systems H and J which had $a_w \simeq 1{\cdot}00$.
[b] Glu, glucose; KS, potassium sorbate; AAs, L-ascorbic acid; ProA, propionic acid; Lys, L-lysine.
[c] Acidification with phosphoric acid.
[d] ** Enough water (W) as to attain 1000 g.
[e] Systems I and J were bottled with headspace.

TABLE 2
Reaction rates and activation energies of L-ascorbic acid destruction and of non-enzymic browning[a]

System	*Storage temp* (°C)	*AAs destruction*[b]			*Non-enzymic browning (NEB)*		
		$(k \pm SD) \times 10^3$ $(1\ h^{-1})$[c]	*n*	E_a[d] $\pm$ *SD* (*kcal mol*$^{-1}$)	$(k \pm SD) \times 10^4$ $(UAb\ h^{-1})$[e]	*n*	E_a[d] $\pm$ *SD* (*kcal mol*$^{-1}$)
A	70	2·5 ± 0·4ACE	8		2·3 ± 0·3ab	7	
	80	6·6 ± 0·1	4	25 ± 3	10·2 ± 0·5c	8	34 ± 2
	90	18·6 ± 0·7BD	7		38·7 ± 0·4d	8	
B	70	3·2 ± 0·2A	7		2·6 ± 0·4a	9	
	80	11·4 ± 0·7	7	27 ± 2	18·3 ± 2·1	8	41 ± 5
	90	30·2 ± 0·2	6		75·2 ± 8·5	8	
C	70	2·8 ± 0·3A	7		12·1 ± 2·5	9	
	80	13·7 ± 0·8	8	35 ± 4	129·0 ± 4·5	10	35 ± 6
	90	49·5 ± 5·2	5		203·3 ± 35·7	8	
D	70	5·0 ± 0·3	5		5·8 ± 1·2	8	
	80	10·0 ± 0·4	6	18 ± 3	30·9 ± 1·1e	10	—
	90	21·8 ± 1·4B	5		29·4 ± 2·0e	7	
E	70	3·0 ± 0·1C	10		2·4 ± 0·2b	12	
	80	11·1 ± 0·1	9	21 ± 3	13·6 ± 1·1c	11	30 ± 4
	90	17·6 ± 0·2D	7		28·8 ± 1·9	9	
F	70	3·0 ± 0·1E	7		4·0 ± 0·4	11	
	80	9·8 ± 0·3	5	27 ± 2	26·1 ± 2·0	14	30 ± 6
	90	27·8 ± 2·4	7		47·0 ± 6·6d	9	
G	70	252·9 ± 15·3	5		206·9 ± 29·4f	10	
	80	731·8 ± 17·4	4	—	227·0 ± 6·5f	4	—
	90	1185·9 ± 198·0	4		632·2 ± 135·1	6	
H	70	1·50 ± 0·17	8		0·50 ± 0·06	10	
	80	5·00 ± 0·08	4	23 ± 3	1·22 ± 0·14	9	—
	90	9·75 ± 0·35	4		1·29 ± 0·19	8	

[a] *k* values with the same following letter are not significantly different (*P*: 0·95).
[b] *k*, reaction rate constant ± SD. (probability level, *P*: 0·95).
[c] Except in system G, which unit is mg% h^{-1} (zero order).
[d] E_a activation energy.
[e] UAb h^{-1}: absorbance unit per hour.

quence, the AAs destruction proceeded mainly through the anaerobic path. Lee *et al* (1977) also observed that oxygen was rapidly depleted in tomato juice packed near anaerobiosis. For that reason, our adjustment excluded the zero time data in those systems stored without headspace. The AAs degradation in that condition could be statistically approximated to first order kinetics, except in the system containing L-lysine where order was approximated to zero value. In accordance with us, many authors have proposed a reaction order of one for AAs anaerobic degradation (Lee *et al* 1977; Nagy and Smooth 1977; Pino and Sánchez Penichet 1981). For each system, rate of degradation enhanced significatively (*P*: 0·95) with temperature.

Non-enzymic browning (NEB) showed a zero order dependence with time when evaluated through absorbance measurement at 420 nm (Table 2).

The relation of kinetic constants to temperature showed, in general, an Arrhenius dependence for the studied systems when calculated according to Labuza and Kamman (1983) and calculated activation energies (E_a) are shown in Table 2.

Effect of pH

Ascorbic acid degradation under anaerobic condition and browning reaction rates increased significantly with the pH in the range 3·5 to 5·0, at 80 and 90°C. Non-enzymic browning (NEB) rates increased also with an increase in pH from pH 4·1 to 5·0 at 70°C (Table 2).

At 80 and 90°C, the pattern of AAs destruction basically agreed with the NEB evolution, while pH increased. No significant differences (*P*: 0·95) were observed between activation energies for AAs degradation as well as for NEB reactions, while pH increases, although a tendency to attain NEB value was observed at the more basic pH for ascorbic acid destruction. The AAs degradation was faster when glucose was present

(compare systems A and H, Table 2) at processing temperatures. Knowing that carbohydrate browning reactions are very active above 70°C and trying to clarify precited fact, in this work, NEB was studied in model systems analogous to those described in Table 1 but, with and without AAs presence. They were stored at a constant temperature of 80°C. Results in Table 3, show us that the AAs presence had a greater influence on browning reactions when glucose was present, as can be seen comparing the parameter k for systems A and H. In this way, it seems to exist an interaction between two browning pathways: that of glucose and that of AAs when both substances are present in the same medium. It must be also remarked that there had been a more significant increase in the browning reactions by effect of the increase in pH, in the system containing glucose when AAs was not present showing a differential influence of pH on glucose caramelization and in glucose-AAs browning. The velocity of the browning reactions for monosaccharides is very slow at pH 3·5 and increases with pH (from 4·1 to 5·0, in our case) because the proportion of the acyclic structure of D-glucose increases (Cerrutti *et al* 1985; Van Dam *et al* 1986). AAs suffers decarboxylation and dehydration and produces 3-deoxypentulose (DP) and then an α,β-non-saturated carbonyl intermediate; 3,4-dideoxy-3-ene-pentulose (DDP) (Kurata and Sakurai 1967a–c).

$$\text{AAs} \rightleftharpoons \text{DP} \longrightarrow \text{DDP}$$

These products are analogous to those that are produced from aldohexuloses (ie D-glucose), by browning reactions.

$$\text{Glucose} \rightleftharpoons \underset{\text{3-deoxyhexulose}}{\text{DH}} \longrightarrow \underset{\text{3,4-dideoxy-3-ene-hexulose}}{\text{DDH}}$$

Davies and Wedzicha (1994), proposed that ascorbate anion can suffer addition through Michael's mechanism (Fodor *et al* 1983), of an α,β-non-saturated carbonyl compound; we propose that 3,4-dideoxy-3-ene-hexulose produced from D-glucose, can act as that carbonyl compound (Fig 1) producing melanoidins. If this reaction proceeds, AAs browning path and glucose browning path affect each other explaining the observed influence (Table 3) of AAs in browning of the system with D-glucose.

Effect of the acid used to adjust pH

Although, for the system with glucose, there is a greater stability of AAs and a lesser NEB at the lower pH, it is also important the acid which is used to adjust pH. AAs loss and NEB rates are greater at 70 and 80°C when phosphoric acid is used (system D) instead of citric acid (A), but no difference is observed at 90°C between both systems.

The citric and the phosphoric acids have complexing action on inorganic metal ions, which can catalyze the AAs degradation and NEB reactions in different conditions (Miller and Joslyn 1949; Furia 1975). The citric acid has a greater complexing capacity than phosphoric acid as can be seen comparing the formation constants in pure water at 25°C of the complexes between these anions and Fe(III) (Burriel Martí *et al* 1985), one of the most common metal ions present as contaminant. In

TABLE 3
Reaction rates at 80°C for non-enzymic browning in model systems with and without AAs

System	*Without AAs*[a]		*With AAs*[a]		$K =$ k with/k without[c]
	$(k \pm SD) \times 10^4$ $(UAb\ h^{-1})^b$	n	$(k \pm SD) \times 10^4$ $(UAb\ h^{-1})^b$	n	
A	4·4 ± 0·3	14	10·2 ± 0·5	14	2·3
B	12·0 ± 2·6	6	18·3 ± 3·9	8	1·5
C	99·5 ± 6·1	14	129·0 ± 7·5	14	1·3
D	12·1 ± 1·0	14	30·9 ± 1·1	13	2·6
E	4·1 ± 0·3	14	13·6 ± 1·1	11	3·3
F	5·5 ± 0·3	14	26·1 ± 2·0	14	4·7
G	252·0 ± 7·2	6	227·0 ± 6·5	6	0·9
H	1·1 ± 0·6	8	1·2 ± 0·1	8	1·1
I	21·7 ± 1·7	14	54·6 ± 4·8	6	2·5
J	4·39 ± 1·9	6	24·2 ± 0·9	5	5·5

[a] k, reaction rate constant ± SD (probability level, P: 0·95).
[b] UAb h^{-1}: absorbance unit per hour.
[c] Relation between browning reaction rate constants with and without L-ascorbic acid added in the system.

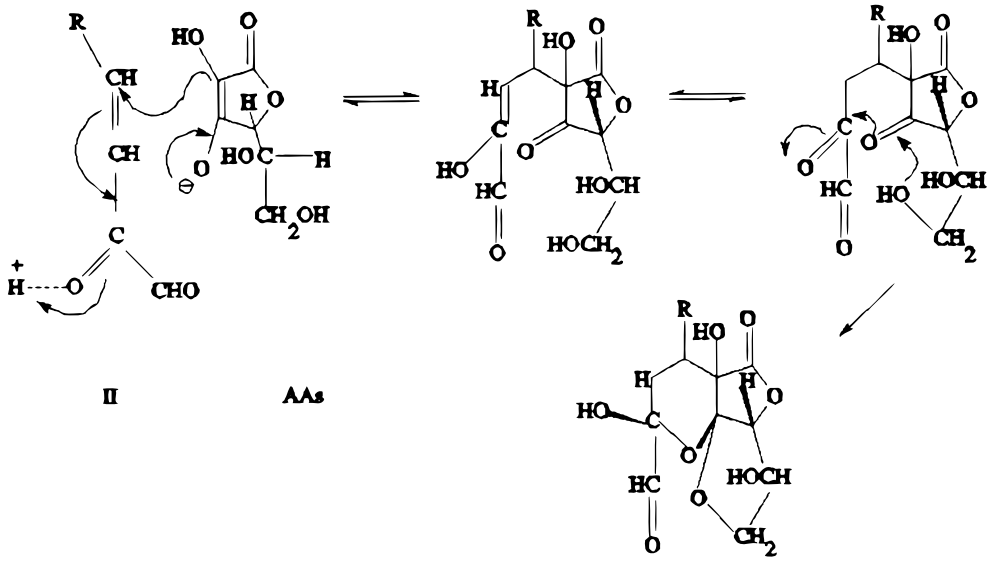


Fig 1. Reaction between ascorbate and α,β-non-saturated carbonyl compound.

Table 4 we can see those constants corrected by pH (3·5) and by the acid reaction of Fe(III) in water. The citrate anion (Cit^{3-}) has a greater complexing effect on Fe(III) than phosphate (PO_4H^{2-}), at pH 3·5 in pure aqueous medium.

Finholt *et al* (1963) found that phosphate buffers accelerate AAs reaction rate, in anaerobic conditions, below pH 6, respect to borate and acetate buffers. Bobbio *et al* (1973) reported that the browning of aqueous solutions with glucose, fructose and xylose, with or without glycine, is greater when phosphate is used for acidification than when citrate is used. Joslyn and Miller (1949) observed that complexing acids protect AAs from its oxidation. In our case, the differential complexing capacity of both acids assayed might be responsible for the different effect observed at 70 and 80°C. The activation energy of AAs destruction was not affected by the change in acid used.

In the study of NEB with or without AAs, at 80°C (Table 3), it could be seen that AAs presence with glucose increases browning in both systems (A and D) in approximately the same grade. The use of phosphoric acid (D) produces the same increase on the rate of NEB when AAs is present or not revealing a net effect of increase of NEB by phosphoric acid.

TABLE 4

Constants of formation in pure water (K_f) of the complexes, at 25°C, modified by the pH (3·5) and by the acidity of the Fe(III) ion (K_f'')

Complex	K_f	K_f'' [a]
$Fe^{3+}/Cit\ H_2^-$	$10^{6\cdot3}$	$5\cdot22 \times 10^4$
$Fe^{3+}/Cit\ H^{2-}$	$10^{11\cdot9}$	$1\cdot18 \times 10^9$
Fe^{3+}/Cit^{3-}	$10^{25\cdot0}$	$2\cdot26 \times 10^{20}$
$Fe^{3+}/PO4H^{2-}$ [a]	$10^{9\cdot4}$	$8\cdot97 \times 10^7$

where

$K_f'' = K_f \cdot \alpha_n \cdot \alpha_{Fe} \quad n = 1, 2, 3$

$\alpha_1 = [Cit\ H_2^-]/C'_A$

$\alpha_2 = [Cit\ H^{2-}]/C'_A$

$\alpha_3 = [Cit^{3-}]/C'_A$

$\alpha_{Fe} = [Fe^{III}]^b/C'_{Fe}$

and

$C'_A = [Cit^{3-}] + [CitH^{2-}] + [CitH_2^-] + [CitH_3]$

$C'_{Fe} = [Fe^{III}] + [Fe(OH)^{2+}] + [Fe(OH)_2^+] + [Fe(OH)_3]$

[a] Form that presents the highest complexing ability at the pH 3·5.

[b] $Fe^{III} = (Fe(H_2O)_6)^{3+}$.

Effect of different antimicrobials

We also studied the differential effect of two antimicrobial additives, at pH 3·5: sorbic and propionic acids. These compounds are very useful in food industry due to their wide spectrum of antimicrobial action at the low pHs, characteristic of fruit juices.

As can be seen in Table 2, no clear effect of sorbic acid replacement by propionic acid was found (systems A and E) with respect to AAs degradation and with respect to NEB in the presence or absence of AAs (Table 3). Not even were found significant differences between activation energies of those systems for precited reactions.

Effect of tin presence

The presence of 10 ppm tin(II) in glucose medium at pH 3·5, was studied. This ion has acid reaction in water, and exists in canned acid fruit juices due to its formation from redox reaction between metal present in the tin coat of the can, and the hydrogen ion present in the acid liquid (Wedzicha 1984; CIEPS, pers comm, 1991).

AAs loss increased with tin(II) presence (system F) at 80° and 90°C, while browning reactions were accelerated significantly in this medium only at 70° and 80°C. Activation energy was not affected by tin presence (Table 2).

In the NEB study at 80°C, with and without AAs addition (Table 3), the presence of tin(II) (F) produced a more important acceleration of the browning reactions when ascorbic acid and glucose were present than when only glucose was. The addition of AAs increased $\simeq 5$ times the NEB reaction rate in system F, while in system A that constant rate increased only twice, due to tin(II) presence. We can conclude that tin(II) exerts an important influence in the browning of glucose-AAs as well as on AAs destruction, at pH 3·5 and at processing temperatures.

Effect of aminoacid

The effect of aminoacid in glucose medium with AAs was evaluated at pH 3·5 (system G). As can be seen in Fig 2, enclosed as an example, L-lysine produced an enhancing effect on AAs degradation and NEB. The kinetic profile of both reactions adjusted statistically to zero order.

In the NEB study at 80°C, with and without AAs addition (Table 3), there was no difference produced by AAs when the aminoacid was present (system G). Probably, Maillard reaction between L-lysine and D-glucose was the principal cause of browning not allowing to appreciate the influence of ascorbic acid presence. The different statistical adjustment of the experimental data for AAs loss in systems containing glucose or glucose and L-lysine, might be caused by the different reactions that proceed when the aminoacid is present, affecting AAs destruction. As can be seen in Fig 3, AAs is involved in different browning reactions (Hodge 1953; Wedzicha 1984; Davies and Wedzicha 1994), according to experimental conditions and the occurrence of one or another can affect AAs kinetic behaviour.

Effect of oxygen presence

The results obtained from the study of oxygen effect on AAs destruction and NEB (systems I and J) are shown in Table 5. Oxidative pathway of AAs destruction prevailed in aerobic condition over non-oxidative one (Kurata and Sakurai 1967a–c), producing a faster AAs degradation and browning development than in systems A and H, bottled without headspace.

Aerobic destruction of AAs adjusted, statistically, to first-order kinetic with respect to AAs. Joslyn and Miller (1949), Blaug and Hajratwala (1972) and Sahbaz and Somer (1993) observed the same reaction order. AAs destruction rate in system containing glucose (I) increased with temperature in the range 70–90°C. In the system without humectants (J), an increment of 20°C was necessary to obtain a significant increase of those reaction rates. The activation energy for AAs loss was smaller when oxygen was present in the system containing glucose (comparing systems I and A, Table 5) showing a smaller sensitivity to temperature.

Glucose (I) diminished AAs oxidation velocity between 70 and 90°C, with respect to the system without humectants (J), while in anaerobic condition the trend observed was the opposite one. Miller and Joslyn (1949) and Joslyn and Supplee (1949) reported the same trend for AAs oxidation comparing AAs oxidation rates and dehydroascorbic acid destruction, in the presence of different carbohydrates and without humectants.

NEB was higher when glucose and oxygen were present (I) only at 80 and 90°C. It must be remembered that the system with glucose (I) had a water activity of 0·94, and the one of system J was 1·00. The results obtained seemed to depend on the balance of the following effects:

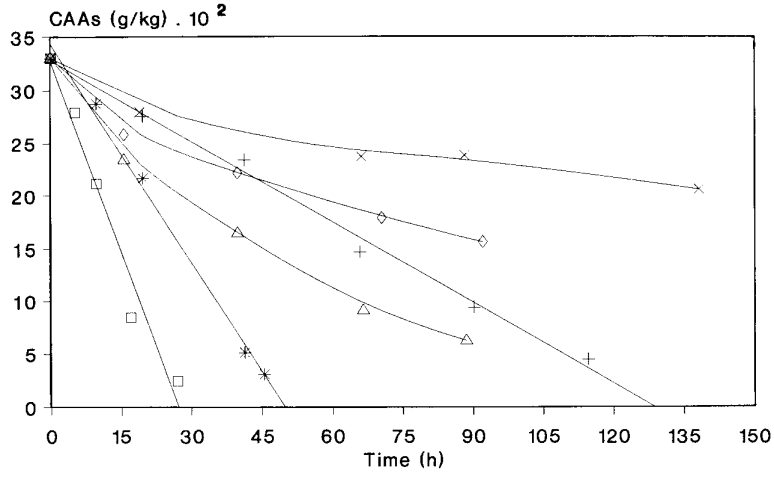


Fig 2. Ascorbic acid destruction in systems containing D-glucose (A) and D-glucose and L-lysine (G). System A: ×, 70°C; ◇, 80°C; △, 90°C. System G: +, 70°C; ∗, 80°C; □, 90°C.

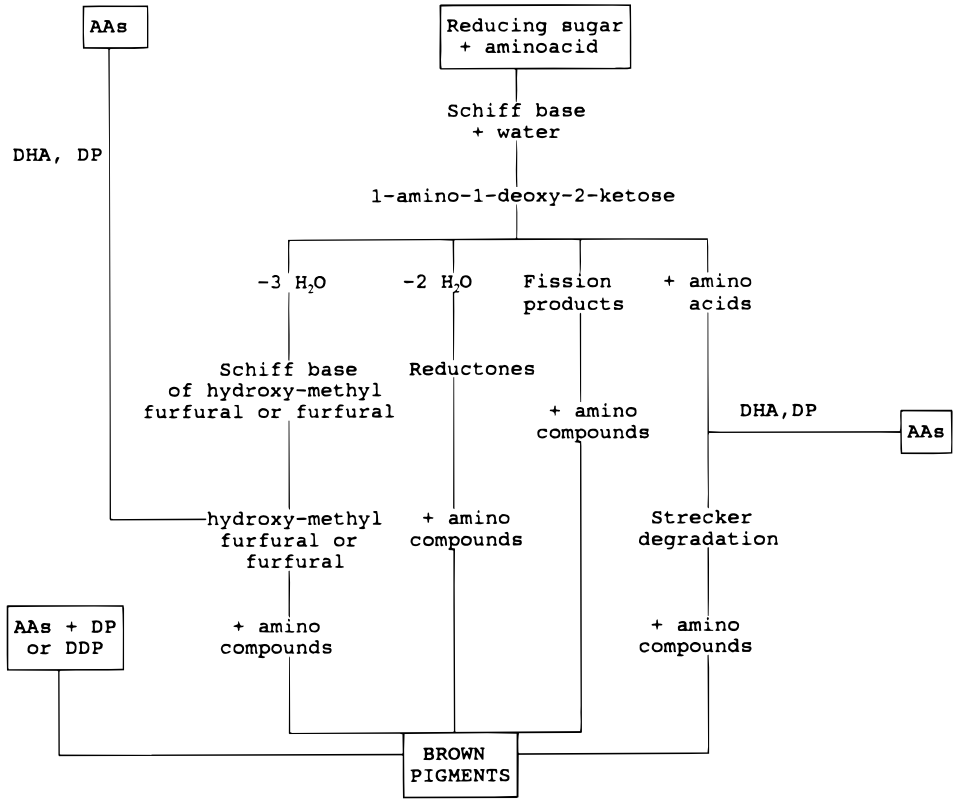


Fig 3. Scheme of non-enzymic browning reactions.

(a) Glucose presence produces an increase in viscosity diminishing oxygen availability. This effect might diminish AAs oxidation rate and consequently, its contribution to NEB.

(b) Viscosity decreases with temperature increase, increasing oxygen availability.

(c) Glucose increases NEB due to its direct contribution to those reactions.

TABLE 5

Reaction rates and activation energies of aerobic L-ascorbic acid destruction and of non-enzymic browning[a]

System	*Storage temp* (°C)	*AAs destruction*[b]			*Non-enzymic browning (NEB)*[b]		
		$(k \pm SD) \times 10^3$ $(1\ h^{-1})$	*n*	E_a [c] $\pm$ *SD* $(kcal\ mol^{-1})$	$(k \pm SD) \times 10^4$ $(UAb\ h^{-1})$[d]	*n*	E_a [c] $\pm$ *SD* $(kcal\ mol^{-1})$
A	70	2·5 ± 0·4	8		2·3 ± 0·2	7	
	80	6·6 ± 0·1	4	25 ± 3a	10·2 ± 0·5	8	34 ± 2
	90	18·6 ± 0·7	7		38·7 ± 0·4	8	
I	70	21·0 ± 1·6	6		9·0 ± 0·5	12	
	80	47·5 ± 1·7	5	14 ± 3	54·6 ± 4·8A	6	—
	90	66·5 ± 3·2	6		51·0 ± 3·2A	8	
H	70	1·5 ± 0·2	8		0·5 ± 0·1	10	
	80	5·0 ± 0·1	4	23 ± 3a	1·2 ± 0·1B	9	—
	90	9·7 ± 0·4	4		1·3 ± 0·2B	8	
J	70	118·2 ± 22·9	4		20·1 ± 1·8C	7	
	80	165·7 ± 15·8	4	—	24·2 ± 0·9C	5	—
	90	216·0 ± 21·3	4		44·5 ± 5·3	8	

[a] *k* with the same letter are not significantly different (*P*: 0·95).
[b] *k*, reaction rate constant ± SD (probability level, *P*: 0·95).
[c] E_a, activation energy.
[d] UAb h^{-1}, absorbance unit per hour.

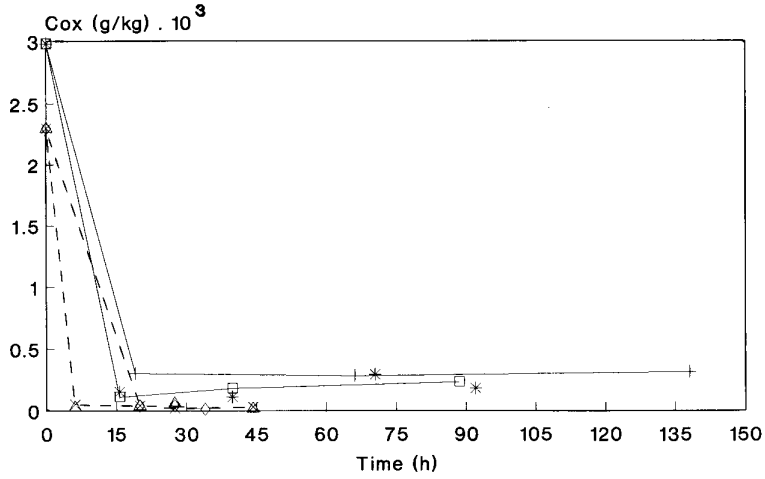
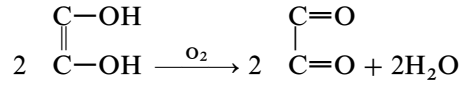


Fig 4. Evolution of dissolved oxygen concentration (corrected at 25°C) in the systems containing glucose package without (A) or with (I) oxygen. System A: +, 70°C; ∗, 80°C; □, 90°C. System I: ×, 70°C; ◇, 80°C; △, 90°C.

(d) Velocity of NEB reaction rises in glucose presence because water activity is depressed from 1·00 to 0·94.

NEB reactions do not depend on oxygen, but oxygen can contribute to browning through production of substances with active carbonyl groups, according to the following reaction:



As can be seen in Table 3, AAs presence produced an increase in browning reaction rates of systems with glucose, bottled with (I) or without (A) headspace (Table 3). However, AAs presence produced a greater acceleration of NEB in control system in aerobic condition (J), with respect to system H probably due to the bigger destruction rate of ascorbic acid in oxygen presence.

Oxygen is a reactive-gas and then it is responsible for a chemical reaction in heterogeneous phase that involves the oxygen diffusion from air-chamber to solution in which ascorbic acid degradation occurs. Different evolution-profiles of dissolved oxygen were observed in systems bottled with headspace according to its composition (Figs 4 and 5). In glucose presence, oxygen profiles were similar in absence or presence of headspace, though AAs degradation in air presence was the fastest. In aerobic condition, the balance of the velocity of oxygen transference and of the velocity of chemical reaction determined the real velocity of AAs loss (Mohr 1980). It must be remembered that the high experimental temperatures used (70–90°C) produced low oxygen solubility and that the high viscosity of glucose medium (system I) made oxygen penetration from gas phase more difficult than in control system (J). Probably, as soon as oxygen from the gas phase dissolved in the liquid phase containing glucose, it was consumed in AAs destruction, resulting a low oxygen

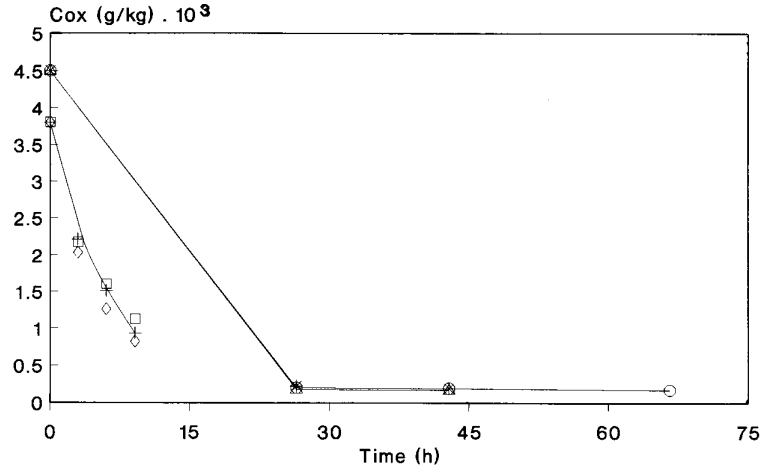


Fig 5. Evolution of dissolved oxygen concentration (corrected at 25°C) in control systems packaged without (H) or with (J) oxygen. System H: ○, 70°C; ∗, 80°C; △, 90°C. System J: □, 70°C; +, 80°C; ◇, 90°C.

residual concentration in the solution along the time of the experiment (Fig 4). In aerobic system without humectants (J), the oxygen profile was different to all other systems. In system without humectants (J), oxygen seemed to be replaced more easily in the liquid phase than in glucose system (I) existing a higher oxygen residual concentration at each time and occurring ascorbic acid loss at a faster rate than in glucose system. As an example, it can be observed that oxygen concentration is 1·5 ppm at 80°C, for a residual AAs concentration of 10·8 mg%, while in the same system bottled without headspace, an oxygen concentration of 0·16 ppm was measured for 13·5 mg% of AAs (Fig 5). Blaug and Hajratwala (1972) studied AAs oxidation between 67 and 85°C in aqueous solution of pHs between 3·52 and 7·22, and ionic strength of 0·4 adjusted with acetate or phosphate buffer. Their results at pH 3·5 were in accordance with ours.

CONCLUSIONS

It should be particularly advantageous to diminish ascorbic acid degradation at thermal processing temperatures (70 to 90°C), in aqueous model system with water activity depressed to 0·94 by glucose, to exclude oxygen and adjust the pH to 3·5 with citric acid. Sorbic or propionic acid can be used as antimicrobial agents in precited conditions. Tin(II), scavenged from coated cans in acid medium, and the presence of L-lysine enhances anaerobic ascorbic acid degradation.

AAs destruction does not always go along with browning development. This behaviour depends on the composition of the system and processing conditions. Anaerobic ascorbic acid destruction parallels NEB reaction at temperatures higher than 70°C. When oxygen is present, the trend is not necessarily the same. For example, glucose presence diminishes ascorbic acid destruction but promotes NEB reactions. It was observed an interaction between glucose and AAs browning pathways based probably in the reaction among DDH and ascorbate anion which might determine a strong influence of their joint presence on browning of the involved systems.

The results reported in this work let us establish some criteria to diminish the AAs degradation and the nonenzymic browning and allow us to choose the components for the formulation of a sweet system with high water activity (0·94), submitted to thermal treatment so as to diminish its nutritional and organoleptic damage during preservation.

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