Interaction Between Potassium Sorbate and Aspartame in Aqueous Model Sugar Systems

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ABSTRACT: The interaction between potassium sorbate and aspartame in aqueous model sugar systems of 0.97 water activity and pH 3.0 was studied. Aspartame addition showed a protective effect over sorbate destruction in an aqueous system of approximately a_w 1, as well as in a system containing glucose; but, in the presence of sucrose, it enhanced degradation. In all systems studied, addition of K sorbate and depression of water activity to 0.97 increased aspartame destruction. The combined use of K sorbate and aspartame exhibited strong nonenzymatic browning potential. The study demonstrated that nonenzynmatic browning can limit shelf life; and it is not recommended to use potassium sorbate together with aspartame.

Key Words: aspartame, sorbates, stability, nonenzymatic browning

Introduction

ASPARTAME, THE METHYL ESTER OF ASPARTYLPHENYLALANINE possesses a clean sweet sugar-like taste with a sweetness potency 200 times that of sucrose (Homler 1984). The use of aspartame has increased in the last decades. It is known that, in the weak acid range of pH 3 to 5, aspartame is more stable than under acid or basic conditions. The stability of aspartame is a function of 3 factors: time, temperature, and pH. The effect of other compounds present is not important (Homler 1984).

Sorbic acid and its potassium salt (K sorbate) are approved as generally recognized as safe additives and are used as antimicrobial agents in a wide range of foods, including low-calorie products. Their inhibitory action is strongly influenced by the type of food, the conditions of processing and storage, and the concentration of the preservative. Sorbates are stable in dry form (McCarthy and Eagler 1976), but in aqueous solutions they suffered an oxidative degradation. Sorbic acid degradation depends on pH, water activity, presence of other additives, conditions of storage, and processing (Gerschenson and Campos 1995; Campos and Gerschenson 1996). It is well known that sorbate degradation in aqueous systems is accompanied by a concomitant increase in the concentrations of carbonyls, mainly acetaldehyde and β-carboxyacrolein, which polymerizes rapidly to brown pigments (Arya and Thakur 1988).

According to Tateo and others (1987), aspartame reacts with carbonyl compounds present in flavoring ingredients of cola-type beverages and also probably reacts with the carbonylic compounds produced after sorbic acid degradation has occurred. There is no information available about the effect of sorbates on aspartame stability or the effect of the latter on sorbates destruction.

We examined the effect of aspartame on sorbic acid stability, the effect of the preservative on aspartame stability, and also the influence of both additives and their destruction on nonenzymatic browning in model aqueous sugar systems of 0.97 water activity and pH 3.0 during storage at 35 °C.

Materials and Methods

THE COMPOSITIONS OF THE DIFFERENT MODEL SYSTEMS ARE given in Table 1. The pH was adjusted to 3.0 by addition of citric acid. Sucrose or glucose concentrations were used to adjust water activity (a_w) to 0.97 (systems D, E, F, G, H, and I). Water activity was measured at 25 °C with a Decagon CX-1 hygrometer (Decagon, Pullman, Wa., U.S.A.).

A volume of 15 mL of each model system was dispensed into stoppered, dark glass flasks and stored at 35 °C (± 1 °C) in forced-convection, constant- temperature chambers. The flasks were hermetically sealed to prevent evaporation.

Each system was stored in duplicate and was sampled at determined intervals. After storage, residual potassium sorbate and/or aspartame content, nonenzymatic browning, pH, and a_w were measured.

Potassium sorbate was measured according to the AOAC (1980) oxidation method that calls for a steam distillation followed by oxidation to malonaldehyde and measurement at 532 nm of the pigment formed between malonaldehyde and thiobarbituric acid. The precision of the technique, evaluated through the coefficient of variance was 3.4% as established previously by Campos and others (1991).

Aspartame was measured by a spectrophotometric method, using ninhydrin as a color reagent and methyl ethyl ketone/ethanol as a solvent mixture (Tuncel and Araman 1989). The reproducibility of the method was approximately 3%.

Nonenzymatic browning was determined by measuring the absorbance at 420 nm (Eichner and Karel 1972). The analysis was performed in a Spekol Zeiss spectrophotometer (Carl Zeiss, Berlin, Germany).

Water activity (a_w) evaluation was used to estimate sucrose hydrolysis considering the effect of glucose and fructose formation in a_w depression (Montes de Oca and others 1991).

All determinations were conducted in duplicate, and in all cases the averages are reported.

Rate constants for sorbic acid, aspartame destruction, and nonenzymatic browning were estimated by linear regression analysis of data. In all cases, the statistical significance of the regressions was evaluated through an analysis of variance. Significant differences among kinetic rate constants were evaluated through a covariance analysis for the equality of the slopes at a 95% confidence level (Sokal and Rohlf 1969).

Table 1—Composition (w/w) of aqueous model systems

Composition (% w/w)	System A	B	C	D	E	F	G	H	I
Potassium sorbate (%)	0.13	0.13	—	0.13	0.13	—	0.13	0.13	—
Aspartame (%)	0.50	—	0.50	0.50	—	0.50	0.50	—	0.50
Sucrose (%)	—	—	—	33.00	33.00	33.00	—	—	—
Glucose (%)	—	—	—	—	—	—	22.00	22.00	22.00
Water (%)	99.37	99.87	99.50	66.36	66.86	66.50	77.36	77.86	77.50
A_w	1.00	1.00	1.00	0.97	0.97	0.97	0.97	0.97	0.97

Table 2—Rate constants of sorbic acid destruction

System	Rate constant [A] $(k \pm e).10^3$ (d^{-1})
A (water/KS/Asp)	35.2 ± 3.0 (a)
B (water/KS)	54.5 ± 6.2
D (water/KS/Asp/Suc)	39.1 ± 1.9 (a)
E (water/KS/Suc)	17.8 ± 1.4 (b)
G (water/KS/Asp/Glu)	36.2 ± 5.5 (a)
H (water/KS/Glu)	81.3 ± 3.9 (b)

k: 1st-order rate constant; e: typical error.
KS: potassium sorbate; Asp: aspartame; Suc: sucrose; Glu: glucose.
[A]: k followed by the same letter is not significantly different (P > 0.05).

Results and Discussion

IN ALL SYSTEMS STUDIED, SORBATES AND ASPARTAME DESTRUCTION exhibited 1st-order and pseudo-1st-order reaction rate constants, respectively, while nonenzymatic browning showed 0-order kinetics. These trends are in agreement with previously published information (Arya 1980; Seow and Cheah 1985; Gerschenson and others 1986; Bell and Labuza 1991a,b; Tsoubeli and Labuza 1991; Thakur and others 1994; Gerschenson and Campos 1995).

Tables 2 and 3 show degradation rate constants for potassium sorbate and aspartame.

Sorbic acid degradation

In the aqueous system of a_w approximately 1 and in the presence of glucose (Table 2, systems B and H), the addition of aspartame showed a protective effect. The protective effect mentioned is in agreement with the findings of Thakur and others (1994), who reported that in the presence of sugars, the amino acids lysine and glycine inhibited the degradation of sorbic acid in aqueous solution. The same effect was observed in the presence of proteins, like beef serum albumin, sodium caseinate, and wheat gluten. This trend was ascribed to the formation of melanoidins, which have been reported to be antitoxigenic in lipid peroxidation activity and to retard rancidity development of foods (Griffith and Johnson 1957; Lingnert and Lundgreen 1980). However, Gerschenson and others (1986) observed that lysine addition to model sugar systems—containing glucose or sucrose with a water activity of 0.94, pH of 3.5, and stored at 20 or 30 °—did not show any effect on preservative degradation.

When sucrose was present, an enhancement in preservative destruction was observed when aspartame was added (Table 2). Probably, in this case, amino acid addition increased sorbate destruction and also decreased the proportion of unsaturated aldehydes due to its role in browning reactions (Arya 1980; Arya and Thakur 1988; Campos and others 1997). As can be seen, depending on system composition, a different effect of aspartame on sorbate stability can be observed.

Water activity depression to 0.97 through glucose or sucrose addition produced no effect on preservative stability when aspartame was present, since rate constants were almost the same for the system free of sugar (A) and for systems containing sucrose or glucose (D and G). This lack of influence on degradation suggested that aspartame exerted a strong action also on nonenzymatic browning, as will be mentioned later, and this action seemed to nullify either the influence of water activity and/or sugar presence.

When systems did not contain aspartame, the effect of a_w depression on sorbate destruction, depended on humectant used. It increased the destruction in the presence of glucose, and it diminished the destruction in the system with sucrose. Different trends were reported about the effect of water activity depression on sorbate destruction. According to Gerschenson and others (1986), an increase in destruction rate was observed when water activity was depressed to 0.94 by the addition of glucose or sucrose in aqueous solutions of pH 3.5. The same trend was observed for fruit squash systems (Thakur and Arya 1991). Conversely, Vidyasagar and Arya (1983) observed a decrease in the destruction rate as a consequence of addition of different levels of sucrose, ranging from 10% to 40% in orange juice. Particularly, in acidic systems containing sucrose the possibility of hydrolysis must be considered with the concomitant change in water activity. In the systems studied containing this sugar (D, E, and F), sucrose hydrolysis proceeded, resulting in a water activity of 0.94 after 20 d of storage instead of the initial value of 0.97, indicating that all the sugar was hydrolyzed. For this reason, in this case, results obtained might be affected by sucrose hydrolysis, concomitant fructose appearance, composition and water activity depression during assay.

Aspartame degradation

It should be noted that less than 50% of the aspartame was destroyed throughout storage. This fact may raise the uncertainty in calculating the order of this reaction (Labuza and Riboh 1982).

In all systems studied, addition of K sorbate enhanced aspartame degradation. This behavior could be explained considering that, under acidic conditions, the loss of aspartame with respect to time can be expressed as:

$$-d\,[APM]\ /\ dt = (k_1 + k_2 + k_3 + k_4)\,[APM]$$

where [APM] is concentration of aspartame; $(k_1 + k_2 + k_3 + k_4)$ is the sum of the observed rate constants for the formation of diketopiperazine (DKP), α-aspartylphenylalanine (α-AP), β-aspartame, and phenylalanine methyl ester (Pme), respectively; and k estimated is $k_1 + k_2 + k_3 + k_4$ (Bell and Labuza 1991a). The conversion of DKP to α-AP is an equilibrium reaction, so the consumption of the product through its reaction with carbonyls produced by sorbic acid degradation via Maillard browning would increase the overall rate of as-

Table 3—Rate constants of aspartame destruction

System	Rate constant [A] $(k \pm e).10^3$ (d^{-1})
A (water/KS/Asp)	5.5 ± 0.5
C (water/Asp)	2.9 ± 0.4
D (water/KS/Asp/Suc)	7.0 ± 0.4 (b)
F (water/Asp/Suc)	4.2 ± 0.4 (a)
G (water/KS/Asp/Glu)	7.2 ± 0.4 (b)
I (water/Asp/Glu)	4.9 ± 0.4 (a)

k: 1st-order rate constant; e: typical error.
KS: potassium sorbate; Asp: aspartame; Suc: sucrose; Glu: glucose.
[A]: k followed by the same letter is not significantly different ($P > 0.05$).

Table 4—Rate constants of nonenzymatic browning

System	Rate constant [A] $(k \pm e).10^3$ (abs/d)
A (water/KS/Asp)	8.5 ± 0.7 (a)
B (water/KS)	1.0 ± 0.1
C (water/Asp)	NBD
D (water/KS/Asp/Suc)	10.0 ± 0.3 (a)
E (water/KS/Suc)	1.9 ± 0.2 (b)
F (water/Asp/Suc)	NBD
G (water/KS/Asp/Glu)	9.3 ± 0.5 (a)
H (water/KS/Glu)	2.5 ± 0.2 (b)
I (water/Asp/Glu)	NBD

k: zero-order rate constant ; e: typical error.
KS: potassium sorbate; Asp: aspartame; Suc: sucrose; Glu: glucose.
[A]: k followed by the same letter is not significantly different ($P > 0.05$).
NBD: no browning detected.

Tabla 5—Time necessary to reach an absorbance at 420 nm of 0.1 in the model systems

System	Time (d)
A (water/KS/Asp)	7.7
B (water/KS)	94.7
C (water/Asp)	NBD
D (water/KS/Asp/Suc)	8.6
E (water/KS/Suc)	48.5
F (water/Asp/Suc)	NBD
G (water/KS/Asp/Glu)	6.0
H (water/KS/Glu)	32.0
I (water/Asp/Glu)	NBD

KS: potassium sorbate; Asp: aspartame; Suc: sucrose; Glu: glucose.
NBD: no browning detected.

partame degradation.

In all systems studied, depression of water activity to 0.97 increased the sweetener destruction, and no differences between glucose or sucrose were detected (systems D, F and G, and I, respectively). Bell and Labuza (1991a) analyzed the influence of water activity on aspartame degradation and reported that an increase in aw from 0.3 to 0.7 resulted in a 30% to 80% increase in degradation rate that then decreased slowly to dilute solution as it was observed in our systems.

It must be remarked that losses of aspartame in our systems ranged from 10% to 30% and that none of the degradation products was sweet. As a consequence, sweetness perception will probably be impaired.

Noenzymatic browning

In the absence of K sorbate, no browning development took place throughout storage (systems C, F, and I), even though both aspartame and sucrose or glucose were present. Stamp and Labuza (1983) reported that an aqueous solution of aspartame, glycerol, and glucose, which has a water activity of 0.8 and a pH of 4.0, showed a shelf life of 60 d at 45 °C (time necessary for the system to reach an absorbance of 0.1). Probably, with the conditions used in this study, the time needed for the development of spectrophotometrically detectable browning will be longer than the one used for the experiment.

For the rest of the systems, browning intensity increased linearly with time, and rate constants are reported in Table 4. It can be seen that addition of aspartame enhanced nonenzymatic browning (compare systems A, D, and G with B, E, and H, respectively). This behavior is expected because nonenzymatic browning via Maillard reaction is one important way of aspartame degradation in foods (Stamp and Labuza 1983), and the production of carbonylic compounds throughout the degradation of sorbate makes possible the development of this reaction. This trend is in agreement with previously published information about the effect of amino acids on the nonenzymatic browning of systems containing K sorbate (Seow and Cheah 1985; Buera and others 1986; Thakur and Arya 1991; Campos and Gerschenson1996). It should be noted that an aqueous solution of the sorbate and aspartame (system A) and systems containing sucrose or glucose (D and G) produced the same extent of browning since no significant differences among rate constants were observed. These results suggest that the Maillard reaction between aspartame and the carbonylic compounds produced by sorbic acid autoxidation is the reaction that posseses the higher browning potential and is the one that governs browning development. Thakur and Arya (1991) and Campos and Gerschenson (1996) also reported the major role of the interaction of degradation products from sorbic acid with amino acids in the browning development.

To illustrate the magnitude of the effect of the interaction between aspartame and the carbonylic products formed by sorbic acid destruction on nonenzymatic browning, Table 5 shows the time necessary to reach an absorbance of 0.1. This value is used as a reference of color spoilage. As it can be seen, in the systems containing potassium sorbate and aspartame (systems A, D, and G), the time necessary to obtain color spoilage was from 5 to 12 times less than the time needed in the system containing K sorbate but without the addition of aspartame.

In the absence of aspartame, occurrence of nonenzymatic browning can be attributed to the polymerization of carbonyls present in sugars or produced by sorbic acid degradation. Water activity depression increased with nonenzymatic browning, and no effect of the humectant used was observed. This trend is in agreement with previous published information about the effect of a slight aw depression in a liquid system (Eichner and Karel 1972). With regard to the fact that browning rate constants were very similar for the systems with glucose and sucrose, this behavior might be expected since the composition of the systems was similar due to complete sucrose hydrolysis after 25 d of storage.

Conclusions

THERE ARE MANY INTERACTIONS BETWEEN POTASSIUM SORbate, aspartame, and other components of a food system. As a result of these interactions, the following took place:

- Sorbic acid stability was improved through aspartame addition in an aqueous solution or when glucose was present. On the contrary, aspartame addition increased degradation when sucrose was present. It is important to take into account that, depending on system composition, if degradation occurs to an important extent, microbiological stability could be affected.

- Aspartame degradation was enhanced by the addition of the preservative and this trend was increased when water activity was depressed to 0.97 by the use of glucose or sucrose. This enhanced degradation might impair sweetening power.
- The interaction of reducing sugars with aspartame did not contribute significantly to the browning development in the systems.
- Aspartame and the carbonyls formed during sorbate degradation react through Maillard mechanism. Under these conditions, off-flavors and undesirable color changes could appear.

The results reported here demonstrate that when low-calorie food formulations are considered, the interactions between additives and/or additives and food ingredients must also be considered. It is not recommended to jointly use potassium sorbate and aspartame, particularly in a low-calorie product where nonenzymatic browning can limit shelf life. This recommendation is based on observations made with aqueous model systems and on the expectation that the same behavior will occur in a food product.

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