

Stability of Sorbic Acid in Aqueous Solutions

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Sorbic acid in aqueous solutions undergoes autoxidation, forming malonaldehyde and other carbonyls. The oxidative degradation follows a first-order reaction kinetics and the rate of reaction decreases with a rise in pH. Amino acids except histidine and arginine increase while NaCl, KCl, sucrose, and trace metal ions (Cu^{2+} ; Fe^{2+} ; Mn^{2+}) decrease the rate of degradation of sorbic acid. Acetic acid, glycerol, and the majority of other salts tested enhance the rate of degradation.

Sorbic acid is widely used as a preservative in fruit juices and bakery and dairy products (Luck, 1976). In this laboratory sorbic acid has been successfully utilized in the preservation of chapaties (Kameshwara Rao et al., 1966; Arya et al., 1977). Being diunsaturated, it is likely to undergo autoxidation in the presence of oxygen. But surprisingly, in dry crystalline form, sorbic acid is highly stable. In solutions and in foods sorbic acid has been reported to undergo autoxidation but the conclusions of various studies are at variance. Steinbach and Franzka (1962) have reported that incorporation of sorbic acid enhanced the rate of autoxidation in butter. Hildegard and Sabalitschka (1965) reported that an aqueous solution of sorbic acid underwent decomposition, forming acrolein, crotonaldehyde, and malonaldehyde. At room temperature $\sim 90\%$ of the sorbic acid was decomposed in 1 year, and the rate of decomposition was inhibited by propyl gallate but accelerated by light. Heintze (1973), however, reported that autoxidation of sorbic acid was not appreciable even after 48 h of intensive aeration. Previously Heintze (1971) has observed that losses in sorbic acid were appreciable in fish sausage but insignificant in fruit juices. Melnick et al. (1954) have, however, claimed that the rate of oxidation of sorbic acid is of the same order of magnitude as that of linoleic and linolenic acids. In preserved chapaties, sorbic acid has been reported to undergo slight degradation, and a possible role of this reaction in the changes in carbonyl profile of chapaties has also been suggested (Arya, 1978). Since a number of factors may participate in the autoxidation of sorbic acid in foods, the effect of pH, temperature, salts, trace metal ions, amino acids, sugar, and glycerol on the stability of sorbic acid in aqueous solutions was studied.

MATERIALS AND METHODS

Reagents. Sorbic acid and amino acids were from E. Merck. All other chemicals were of analytical reagent grade and used as such without further purification. Methyl alcohol and ethyl alcohol were refluxed with aluminum dust and potassium hydroxide and distilled to make them free from carbonyls.

Storage Tests. Four milliliters of ethanolic solution of sorbic acid (10% w/v) was diluted to 200 mL with distilled water and stored in 500-mL glass stoppered flasks at 30, 37, and 46 °C. Required quantities of amino acids, salts, sugar, glycerol, alcohol, acetic acid, and propyl gallate were added to the sorbic acid solution before making up the final volume to 200 mL. Freshly prepared sorbic acid (0.2% w/v) has a pH of 3.3, and this was adjusted from 2.6 to 7.0 with a few drops of hydrochloric acid or sodium hydroxide solution. Every day the stoppers of the flasks

were removed and the contents vigorously swirled to replenish the oxygen consumed during the reaction. Initially and periodically the absorbance at 258 nm, total carbonyls, and malonaldehyde content of stored solutions were measured after appropriate dilutions. Total carbonyls were measured according to Sanders and Schubert (1971) by using 0.1 N HCl instead of 0.01 N HCl as given in the procedure. Malonaldehyde content was measured by treating 5 mL of sorbic acid solution with 5 mL of aqueous thiobarbituric acid (TBA) solution (0.5% w/v), heating the reaction mixture in boiling water for 30 min, and measuring the color intensity at 530 nm. Formation of malonaldehyde in stored sorbic acid solution was established from the absorption maxima (532 nm) of the colored complex formed with thiobarbituric acid and by comparing the R_f value of the TBA chromogen with that obtained from tetramethoxypropane by using descending paper chromatography and the upper phase of the solvent mixture of phenol-2-propanol-formic acid-water (80:10:10:100) as the irrigating solvent (Sinnhuber et al., 1958).

RESULTS AND DISCUSSION

Sorbic acid in aqueous solution has a strong absorption maxima at 258 nm ($E_{1\%}^{258}$ 2150) due to the conjugated double bond carbonyl system in its molecule. During storage, the intensity of this maxima decreased considerably and a new, very weak absorption maxima appeared between 215 and 225 nm (Figure 1). After 17 days of storage at 37 °C, $E_{1\%}^{258}$ decreased from 2150 to 800. Decreases in absorbance at 258 nm were accompanied by simultaneous increases in total carbonyls and malonaldehyde content and a slight decrease in pH (Figure 2). Increase in total carbonyls was found to be significantly correlated ($r = -0.91$) with the changes in absorbance at 258 nm. Accordingly, autoxidative degradation of sorbic acid in aqueous solution may be followed by measuring changes in total carbonyls and absorbance at 258 nm. In the presence of amino acids, however, carbonyls undergo further condensation reactions, forming brown pigments, and their concentration does not correlate with the degradation of sorbic acid. The concentration of malonaldehyde increased initially until $\sim 60\%$ of the sorbic acid was degraded, but its concentration commenced to decrease during subsequent storage (Figure 2). Though Melnick et al. (1954) had reported the formation of hydroperoxides in autoxidizing sorbic acid in nonaqueous systems, these did not accumulate at measurable levels in aqueous solutions.

In the present study degradation of sorbic acid was followed by measuring absorbance at 258 nm, and the concentration of unreacted acid was calculated from absorbance values and the molar extinction coefficient (E_M^{258} 24 080) of sorbic acid. Typical plots of logarithm of sorbic acid concentration vs. storage period are given in Figure 3. It may be observed that degradation of sorbic acid in

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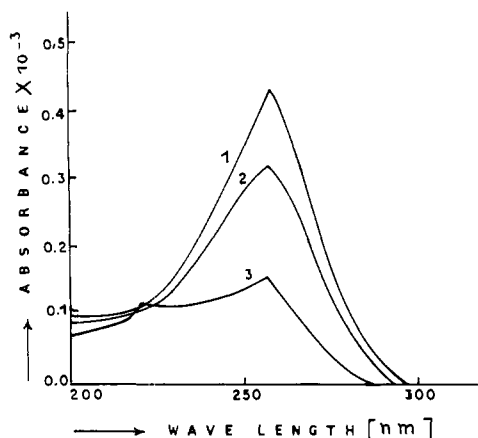


Figure 1. Changes in absorption spectra of aqueous sorbic acid solution (0.2%; pH 3.3) during storage at 37 °C. (1) Fresh; (2 and 3) after 9 and 17 days of storage, respectively. Absorbance was measured after 1000-times dilution; pH of the diluted solution was 5.8.

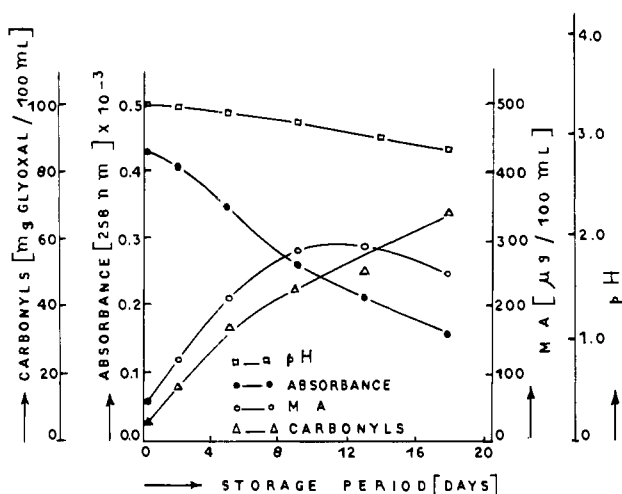


Figure 2. Changes in pH, total carbonyls, absorbance, and malonaldehyde content in aqueous solutions of sorbic acid at 37 °C.

Table I. Effect of Temperature and pH on the Rate of Degradation of Sorbic Acid in Aqueous Solutions

reaction conditions		rate constant (K_{obsd}) $\times 10^3$, h^{-1}
temp, °C	pH	
30	3.3	1.15 \pm 0.05
37	3.3	2.10 \pm 0.06
46	3.3	2.95 \pm 0.10
37	2.6	2.75 \pm 0.09
37	3.6	0.70 \pm 0.04
37	4.0	0.18 \pm 0.02
37	4.6	0.12 \pm 0.02
37	5.0	0.09 \pm 0.02
37	7.0	0.03 \pm 0.01

aqueous solutions follows a first-order or pseudo-first-order reaction kinetics and the rate of reaction is very much dependent on the temperature and hydrogen ion concentration (Table I). The reaction, however, does not follow the Arrhenius equation, a characteristic of the majority of free radical reactions. The rate of reaction decreases with an increase in pH and becomes negligible above a pH of 5.0. Since the pK_a of sorbic acid is 4.75, it would suggest that only undissociated sorbic acid molecules are susceptible to oxidative degradation in aqueous solutions; ionized molecules are degraded to a negligible extent. Previously Mabrouk and Dugan (1960) have also observed that oxi-

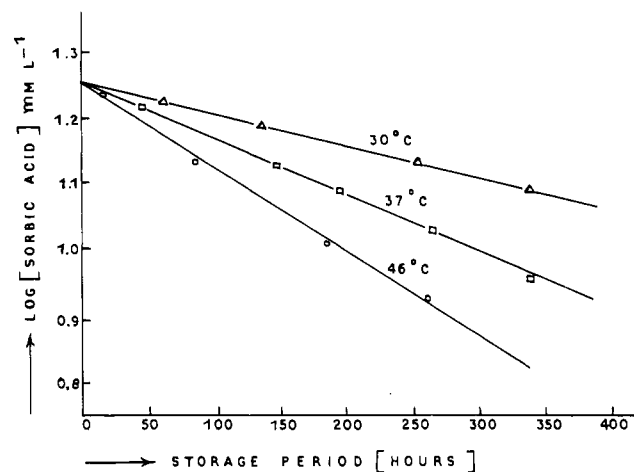


Figure 3. Effect of temperature on the degradation of sorbic acid.

Table II. Effect of Amino Acids (1×10^{-3} mol/100 mL) on the Rate of Degradation of Sorbic Acid (SA) in Aqueous Solutions at 37 °C

amino acid	pH	rate constant (K_{obsd}) $\times 10^3$, h^{-1}
SA	3.3	2.10 \pm 0.06
SA plus Gly	3.5	2.25 \pm 0.08
SA plus Ala	3.4	2.78 \pm 0.09
SA plus Phe	3.5	2.42 \pm 0.09
SA plus Ser	3.4	2.66 \pm 0.10
SA plus His	4.9	1.20 \pm 0.05
SA plus His ^a	3.3	2.40 \pm 0.06
SA plus Arg	4.9	0.50 \pm 0.05
SA plus Arg ^a	3.3	2.12 \pm 0.08
SA plus Asp	3.3	2.48 \pm 0.08
SA plus Cys-HCl	2.8	2.71 \pm 0.10
SA plus Lys-HCl	3.4	2.61 \pm 0.12

^a The pH of the reaction mixtures was adjusted to 3.3 with dilute HCl.

dation of linoleate increases with decreasing pH values.

The effect of various amino acids on the rate of degradation of sorbic acid is shown in Table II. It may be seen that except for histidine and arginine all other amino acids investigated enhanced the rate of degradation. Both histidine and arginine, on the other hand, considerably stabilized sorbic acid in aqueous solutions. Addition of histidine and arginine to an aqueous sorbic acid solution (0.2%) enhanced its pH from 3.3 to 4.9, and adjustment of the pH of the reaction mixtures back to 3.3 with HCl completely eliminated the stabilizing action of both histidine and arginine (Table II). Apparently, in aqueous solutions, the carboxyl group of sorbic acid forms a salt linkage with the basic nitrogen atom in the amino acid molecule. This will enhance the ionization of sorbic acid and thereby its stability. At lower pH values, nitrogen atoms in amino acid molecules already exist in protonated form and thereby are unable to form a salt linkage with sorbic acid.

Addition of amino acids considerably enhanced the rate of browning but significantly reduced the accumulation of total carbonyls and MA in the sorbic acid solution during storage (Table III). This is in conformity with the published information that, in the presence of amino acids, carbonyls are known to further undergo aldol-type condensation, resulting in brown pigments (Arya and Parihar, 1977).

The effects of various salts and trace metal ions on the stability of sorbic acid are shown in Tables IV and V, respectively. Addition of NaCl and KCl considerably enhanced whereas LiCl and NH_4Cl significantly reduced the

Table III. Effect of Amino Acids (1×10^{-3} mol/100 mL) on Changes in Total Carbonyls and Browning Intensity during Storage of Aqueous Solutions of Sorbic Acid (SA)

additive	total carbonyls, mg of glyoxal/100 mL, after				browning intensity (absorbance at 400 nm), after			
	0 days	5 days	9 days	13 days	0 days	5 days	9 days	13 days
SA	1.5	24.6	40.0	52.6	0.01	0.04	0.09	0.14
SA plus Gly		15.6	22.8	38.7		0.15	0.33	0.54
SA plus Ala		16.9	24.9	49.3		0.13	0.22	0.32
SA plus Phe		16.0	22.6	39.2		0.14	0.29	0.46
SA plus Ser		15.4	23.0	40.3		0.11	0.20	0.36
SA plus Asp		15.8	20.5	39.0		0.19	0.35	0.56
SA plus His		6.8	8.7	19.2		0.20	0.30	0.43
SA plus Arg		5.8	7.9	18.7		0.15	0.26	0.39
SA plus Cys-HCl		3.0	6.8	18.5		0.22	0.38	0.60
SA plus Lys-HCl		18.6	23.9	38.7		0.18	0.31	0.45

Table IV. Effect of Some Salts on the Degradation of Sorbic Acid (SA) in Aqueous Solutions at 37 °C

salt	pH	rate constant ($K_{\text{obsd}} \times 10^3, \text{h}^{-1}$)
SA	3.3	2.10 ± 0.06
SA plus NaCl (0.1%)	3.3	1.24 ± 0.03
SA plus NaCl (0.5%)	3.3	0.61 ± 0.03
SA plus NaCl (2%)	3.3	0.14 ± 0.02
SA plus KCl (2%)	3.3	0.45 ± 0.04
SA plus LiCl (2%)	3.3	3.33 ± 0.10
SA plus Na ₂ SO ₄ (2%)	3.4	4.26 ± 0.10
SA plus K ₂ SO ₄ (2%)	3.4	4.26 ± 0.11
SA plus (NH ₄) ₂ SO ₄ (2%)	3.5	4.35 ± 0.10
SA plus Na ₂ HPO ₄ (2%)	4.0	1.77 ± 0.06
SA plus Na ₃ PO ₄ (2%)	7.5	0.04 ± 0.01

Table V. Effect of Some Metal Ions (50 ppm) and Propyl Gallate (PG) on the Stability of Sorbic Acid (SA) in Aqueous Solutions at 37 °C

metal ion	rate constant ($K_{\text{obsd}} \times 10^3, \text{h}^{-1}$)
SA	2.10 ± 0.05
SA plus Fe ²⁺	0.12 ± 0.02
SA plus Cu ²⁺	0.08 ± 0.01
SA plus Mn ²⁺	0.07 ± 0.01
SA plus Ni ²⁺	2.15 ± 0.05
SA plus Zn ²⁺	2.08 ± 0.06
SA plus PG (0.01%)	0.09 ± 0.02

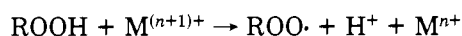
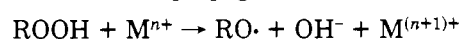
stability of sorbic acid in aqueous solutions. The protective effect of NaCl and KCl increased as the concentration of salt was increased from 0.1 to 2%. Sulfates of Na⁺, K⁺, and NH₄⁺ all exhibited a strong prooxidant effect in the degradation of sorbic acid in aqueous solutions. The effect of phosphate ions is more complex. Addition of Na₂HPO₄ and Na₃PO₄ increases the pH of the reaction mixture which has a stabilizing effect. But when the pH was adjusted back to 3.3 or when the rate is compared at a same pH level (Tables I and IV), phosphate ions exhibit a definite prooxidant effect in the degradation of sorbic acid. This is quite surprising because both citric and phosphoric acids are widely used in the stabilization of fats and oils for their ability to complex with trace metal ions (Fe⁺, Cu⁺, etc.) which have pronounced catalytic action in the autoxidation of unsaturated fatty acids. On the other hand, the role of trace metal ions in the degradation of sorbic acid is very complex. While Cu²⁺, Fe²⁺, and Mn²⁺ exhibited a very pronounced stabilizing effect, Ni²⁺ exhibited a slight catalytic action but Zn²⁺ had no significant effect on the stability of sorbic acid in aqueous solutions. As expected, propyl gallate exhibited a very strong inhibitory effect in the oxidative degradation of sorbic acid. The above conclusions are also supported by the changes in total carbonyls taking place in autoxidizing sorbic acid solutions (Table VI). Previously Tappel (1955) has ob-

Table VI. Effect of Metallic Ions (50 ppm) and Propyl Gallate (PG) (100 ppm) on the Changes in Carbonyls in Sorbic Acid Solutions during Storage

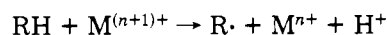
additive	carbonyls, mg of glyoxal/ 100 mL, after				
	0 days	5 days	12 days	19 days	26 days
SA	1.8	25.5	49.2	65.8	70.3
SA plus Cu ²⁺		2.0	2.5	2.5	3.0
SA plus Fe ²⁺		3.0	3.5	4.0	5.4
SA plus Mn ²⁺		1.0	1.2	1.5	2.6
SA plus Ni ²⁺		30.5	55.6	69.8	76.3
SA plus Zn ²⁺		24.5	48.3	64.3	68.8
SA plus PG		2.0	2.5	2.5	5.1

served that haematin considerably reduced the rate of oxygen absorption by sorbic acid.

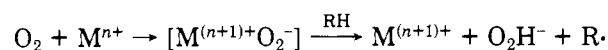
The role of metal catalysis in the autoxidation of organic compounds in liquid phase has been discussed by Ingold (1961). Heavy metal ions, especially those possessing two or more valency states with a suitable oxidation-reduction potential between them, generally accelerate the rate of autoxidation. This is mainly due to their ability to decompose hydroperoxides into free radicals which accelerates the rate of chain propagation:



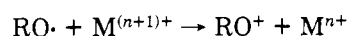
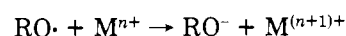
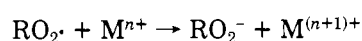
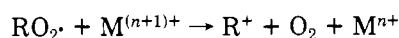
Heavy metal ions may also accelerate autoxidation by participating in the initiation reactions, and in fact it has even been suggested that initiation of autoxidation of even highly purified fats/oils may be due to metal catalysis (Uri, 1956):



or



On the other hand, it has also been suggested (Ingold, 1961) that under certain conditions heavy metal ions may decrease the rate of autoxidation either by forming stable complexes with free radicals or by destruction of free radicals through the reactions



Since the autoxidation of conjugated polyunsaturated fatty acids is reported to proceed through the formation of bi-radicals (Allen and Kummerow, 1951), it is most likely that

Table VII. Effect of Sucrose, Glycerol, Acetic Acid, and Alcohol on the Rate of Degradation of Sorbic Acid (SA) at 37 °C

additive	rate constant ($K_{\text{obsd}} \times 10^3, \text{h}^{-1}$)
SA	2.11 ± 0.06
SA plus sucrose (1%)	2.11 ± 0.06
SA plus sucrose (5%)	2.08 ± 0.05
SA plus sucrose (10%)	1.78 ± 0.04
SA plus acetic acid (5%)	2.88 ± 0.08
SA plus glycerol (1%)	2.18 ± 0.08
SA plus glycerol (5%)	2.20 ± 0.06
SA plus ethyl alcohol (10%)	2.10 ± 0.05
SA plus ethyl alcohol (25%)	2.09 ± 0.04

the decreased rate of autoxidation of sorbic acid in the presence of Cu^{2+} , Fe^{2+} , and Mn^{2+} results from the ability of these ions to form complexes with peroxy biradicals. The extent of stabilization by different metals may be determined by their ability to form complexes and the stability of these complexes. However, presence of these complexes in autoxidizing sorbic acid remains to be elucidated.

The effect of sucrose, glycerol, acetic acid, and the ethyl alcohol in the degradation of sorbic acid is shown in Table VII. In low concentrations (<5%), sucrose did not significantly influence but in higher concentrations it significantly reduced the rate of degradation. Glycerol, on the other hand, showed a slight but significant prooxidant effect. Sims et al. (1978) have observed that sugars and sugar alcohols inhibit autoxidation of safflower oil in emulsions. These workers have claimed that in viscous emulsions, the migration of oxygen through the aqueous layer becomes the rate-limiting step in the autoxidation of the lipid phase. In the present study, however, glycerol showed a slight catalytic effect at both the 1% and 5% levels but sucrose exhibited an inhibitory action at the 10% level. Addition of acetic acid considerably enhanced whereas ethyl alcohol (<25%) had practically no effect on the oxidative degradation of sorbic acid in aqueous solutions.

From the foregoing discussion, it is evident that a number of factors such as pH, temperature, trace metal ions,

salts, amino acids, and other food additives considerably influence the stability of sorbic acid in aqueous systems. The mechanism of autoxidative degradation of sorbic acid in aqueous systems seems to differ considerably from that of normal autoxidation of naturally occurring nonconjugated polyunsaturated fatty acids.

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