storage roots showed a greater amount of accumulation with FSN fertilization. Thus, the absorption patterns of these elements for the two vegetable crops require further study.

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Stability of Sorbic Acid in Orange Squash

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Degradation of sorbic acid (SA) in orange squash was appreciable when stored in polypropylene pouches but very slight when stored in laminate pouches and glass bottles. In model systems also, the degradation of SA was high in polyethylene and polypropylene pouches but negligible in saran-coated cellopoly and laminate pouches. Metabisulfite and fruit acids acted as prooxidants while sucrose above 5% decreased the rate of degradation.

Use of sorbic acid (SA) as an antimicrobial food additive is permitted in many countries, and it is extensively used in preserving fruit juices, bakery, and dairy products. Though information on the physiological harmlessness of SA is well documented, literature on its stability in foods during processing and storage is at variance. Arya (1980) reported that in aqueous solution SA undergoes autoxidative degradation, forming malonaldehyde and other carbonyls. The degradation was found to be influenced by a number of factors such as temperature, pH, and the presence of salts, trace metal ions, glycerol, and amino acids. Bolin et al. (1980) have also reported degradation of SA during storage of raisins, the losses being related with storage temperature and moisture content. Heintze (1973), however, reported that autoxidation of SA was not appreciable even after 48 h of intensive aeration. Heintze (1971) had reported that degradation of SA was appreciable in fish sausages but insignificant in fruit juices. In none of these studies has the role of packaging material on the rate of degradation of SA been evaluated. In the present paper the stability of SA in orange squash and the role of packaging materials and squash ingredients are described.

MATERIALS AND METHODS

Reagents. Sorbic acid and potassium sorbate 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 for 2 h and distilled in an all-glass apparatus to free them from traces of carbonyls.

Orange Squash. Good-quality mandarin oranges (*Citrus reticulata*) procured from a local market were washed under running water and peeled, and the rag sticking to the segments was removed by hand. The segments were passed through a laboratory model stainless steel screw-type juice extractor (Raylon Metal Works, Bombay, India). Freshly extracted juice had a Brix of 9° and titratable acidity of 0.63%. The orange squash was prepared by mixing cane sugar (8.0 kg), citric acid (177 g), and water (2 L) with 10 kg of freshly extracted juice. Freshly prepared squash on analysis gave 45 °Brix and 1.2% titratable acidity. The squash was pasteurized by heating it in a stainless steel vessel for 10 min in a thermostatically controlled water tank maintained at 80 ± 2 °C. The juice was continuously stirred during the heating operation and attained bath temperature in 8 min. After pasteurization the juice was cooled, divided into four lots, and separately treated with (a) 0.061% potassium metabisulfite (350 ppm of SO_2), (b) 0.035% potassium metabisulfite (200 ppm of SO_2) plus 0.268% potassium sorbate (0.2% SA), (c) 0.134% potassium sorbate (0.1% SA), and (d) 0.268% potassium sorbate (0.2% SA).

Storage Tests. The treated squash samples were stored in hermetically sealed pouches (6 in. × 4 in.) of polypropylene (60 μm) and paper (60 g)-Al foil (40 μm)-

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Table I. Stability of Sorbic Acid in Orange Squash during Storage at 37 ± 1 °C

| | | concentration of sorbic acid, %, after | | | | | |
| | | 60 days | | | 120 days | | |
treatment	0 days	polypro-pylene	paper–Al foil–poly-ethylene laminate	bottle	polypro-pylene	paper–Al foil–poly-ethylene laminate	bottle
potassium sorbate (0.268%)	0.20	0.12	0.19	0.18	0.07	0.16	0.16
potassium sorbate (0.134%)	0.10	0.04	0.09	0.09	0.02	0.08	0.08
potassium sorbate (0.268%) + potassium metabisulfite (0.035%)	0.20	0.15	0.19	0.18	0.08	0.16	0.17

polyethylene (40 μm) laminate and also in glass bottles at room temperature (15–30 °C) and 37 ± 1°C away from direct fluorescent light or sunlight.

Isolated Systems. Four milliliters of ethanolic solution of SA (10% w/v) were diluted to 200 mL with distilled water and stored in stoppered flasks at 37 ± 1 °C. Required amounts of acids (0.05 mol; oxalic, succinic, citric, lactic, tartaric, maleic, fumaric, and malic acids), sugar (5–40% w/v), and potassium metabisulfite (250–1000 ppm as SO_2) were added to the SA solution before making up the final volume to 200 mL. Every day the stoppers of the flasks were removed and the contents thoroughly swirled to replenish the oxygen consumed during the reaction.

Similarly, 50-mL aliquots of SA solution (0.2% w/v) were stored in hermetically sealed pouches of polyethylene (75 and 175 μm), polypropylene (60 μm), saran [poly(vinylidene chloride)]-coated cellopoly (75 μm), and paper–Al foil–polyethylene laminate at 37 ± 1 °C to evaluate the role of packaging materials in the degradation of SA.

Analysis. SA in orange squash was determined spectrophotometrically by the method of Alderton and Lewis (1958) with slight modifications. Accurately weighed amounts of orange squash containing 1–2 mg of sorbic acid were treated with 50 mL of 0.1 N H_2SO_4 and 50 g of magnesium sulfate. The mixture was steam distilled and 350 mL of the distillate was collected. After the pH was adjusted to 5.0, the volume was made to 500 mL and absorbance measured at 258 nm. The SA concentration was calculated from absorbance values by using an $E_{1cm}^{1\%}$ of 2150 and expressed as percent SA. The average recovery of SA in this method was 98 ± 2%.

Changes in the SA concentration in isolated systems were followed by measuring their abosrbance at 258 nm after appropriate dilutions. Sulfur dioxide and titratable acidity (expressed as percent citric acid) were determined by AOAC procedures (1970) while total carbonyls were measured by the method described by Arya (1980). Brix readings were measured at 25 °C with a hand refractometer.

RESULTS AND DISCUSSION

The changes in the concentration of SA in orange squash during storage at 37 °C are shown in Table I. It may be observed that SA degradation was highest in polypropylene pouches. Loss of SA in polypropylene pouches ranged from 60 to 80% compared to 15 to 20% in glass bottles and laminate pouches after 120 days of storage at 37 °C. Under ambient storage also, losses were considerably higher (30–36%) in polypropylene pouches than in glass bottles and laminate pouches (12–15%) after 120 days of storage. Clearly, packaging materials play a major role in the degradion of SA in orange squash. Glass bottles and laminate pouches, being impermeable to oxygen, retained a major portion of added SA. Slight losses observed in SA concentration in these packages are brought about by the dissolved and headspace oxygen. On the other hand, owing to high oxygen permeability of polypropylene film, oxygen

Table II. Effect of Packaging Material on the Rate of Degradation of Sorbic Acid in Aqueous Solutions at 37 ± 1 °C

packaging material	rate constant, $K_{obsd} \times 10^3$, h^{-1}
polyethylene (75 μm)	5.45 ± 0.16
polyethylene (175 μm)	4.87 ± 0.18
polypropylene (60 μm)	3.89 ± 0.18
high-density polyethylene (75 μm)	3.90 ± 0.20
saran-coated cellopoly (75 μm)	0.09 ± 0.008
paper–Al foil–polyethylene laminate	0.06 ± 0.009

Table III. Formation of Carbonyls in Aqueous Solution of Sorbic Acid during Storage at 37 ± 1 °C

| | total carbonyls, mg of glyoxal/100 mL, after | | | | |
packaging material	0 days	5 days	7 days	10 days	21 days
polyethylene (75 μm)	0.12	1.90	6.75	7.50	17.10
polyethylene (175 μm)		1.43	5.44	7.50	15.97
polypropylene (60 μm)		1.23	4.33	6.10	12.00
high-density polyethylene (75 μm)		1.28	5.74	6.77	13.90
saran-coated cellopoly (75 μm)		0.33	0.48	0.94	0.94
paper–Al foil–polyethylene laminate		0.14	0.20	0.24	0.26

concentration in orange squash in polypropylene pouches does not become rate limiting in SA oxidation. Oxidation of SA, therefore, continues until it is depleted from the system. The relationship between oxygen permeability of the packaging material and SA degradation was also confirmed in isolated systems. For this purpose an aqueous SA solution was stored in pouches made from different films having varying oxygen permeabilities. It is interesting to note (Table II) that rate of SA degradation is negligible in saran-coated cellopoly and laminate pouches compared to polyethylene and polypropylene pouches. The above conclusions are also supported by the changes in the carbonyls in autoxidizing SA solution (Table III). It may be observed that formation of carbonyls is highest in polyethylene and polypropylene pouches, which have high oxygen permeabilities, but practically insignificant in laminate pouches. Previously, Arya (1980) has reported that formation of carbonyls in autoxidizing SA solutions is significantly correlated (r = –0.91) with SA degradation. Hildegard and Sabalitschka (1965) have also reported the formation of crotonaldehyde, acrolein, and malonaldehyde from SA degradation in aqueous solution.

Sulfur dioxide either alone or in combination with benzoate and sorbate is widely used in the preservation of fruit juices. Its role in the degradation of SA is rather complex. While in isolated systems, addition of metabisulfite significantly accelerated the rate of degradation of SA (Table IV), which is also supported by a higher rate of formation of carbonyls (Table V). The increase in carbonyls in samples having metabisulfite was, however, not in direct proportion to the increase in rate constant.

Table IV.   Effect of Sulfur Dioxide on the Rate of Degradation of Sorbic Acid in Aqueous Solution Stored at 37 ± 1 °C

sulfur dioxide, ppm	rate constant, $K_{obsd} \times 10^3$, h^{-1}
0	2.15 ± 0.26
250	4.22 ± 0.29
500	4.74 ± 0.27
750	5.42 ± 0.32
1000	6.07 ± 0.34

Table V.   Effect of Sulfur Dioxide on the Changes in Carbonyls in Sorbic Acid Solution during Storage at 37 ± 1 °C

sulfur dioxide, ppm	carbonyls, mg of glyoxal/100 mL, after 4 days	carbonyls, mg of glyoxal/100 mL, after 24 days
0	2.64	5.68
250	4.21	6.98
500	4.21	9.74
750	4.72	9.75
1000	5.12	10.86

This is expected because bisulfite is known to form addition products with carbonyl compounds. Prooxidant action of sulfite has been reported by Lizada and Yang (1981) in the autoxidation of linoleic and linolenic acids, Beard et al. (1972) in the oxidation of orange oil, and Peiser and Yang (1979) in the autoxidation of β-carotene. It has been suggested that the catalytic action of sulfite is mediated through the formation of SO_3^{2-} and ·$RHSO_3^-$ radicals.

But in orange squash addition of metabisulfite did not significantly influence the storage degradation of SA (Table I). In orange squash stored in polypropylene pouches, no SO_2 could be detected after 120 days of storage. But in bottles and laminate pouches its level ranged from 125 to 128 ppm after 60 days and from 60 to 65 ppm after 120 days of storage at 37 °C. Evidently, a large portion of added SO_2 is lost during the early stages of storage either due to oxidation or through its reaction with other constituents. Besides, SO_2 is also known to form reversibly addition products with aldehydes, ketones, and reducing sugars. A detailed study of the reaction equilibrium between D-glucose and SO_2 in aqueous solutions has been made by Vas (1949) and binding of SO_2 with orange juice constituents has been reported by Ingram and Vas (1950a,b). Formation of bisulfite adjucts has been reported to be pH dependent, and the importance of this reaction in foods has been discussed by Green (1976) and Gehman and Osman (1954). It has been suggested that a major portion of SO_2 in orange juice and sugar solutions exists in bound form as the bisulfite adduct, which is unable to participate in free radical reactions. Apparently, the concentration of SO_3^{2-} capable of catalyzing lipid peroxidation is not large enough in orange squash to have a significant catalytic effect in SA oxidation.

The effect of sugar concentration in the degradation of SA is shown in Table VI. The results of the present study confirm the previous observation (Arya, 1980) that in low concentrations (<5%) sugar does not significantly influence but in higher concentrations (>10%) it considerably reduces the rate of SA degradation. In fruit squashes where the sugar concentration is about 45%, it will definitely have a stabilizing effect. Sims et al. (1978) have reported that sugars and sugar alcohols inhibit autoxidation of safflower oil by decreasing the rate of migration of oxygen through the aqueous layer. The concentration dependent inhibitory effect of sugar as observed

Table VI.   Effect of Sucrose on the Rate of Degradation of Sorbic Acid in Aqueous Solutions at 37 ± 1 °C

sucrose, %	rate constant, $K_{obsd} \times 10^3$, h^{-1}
0	2.15 ± 0.18
5	2.07 ± 0.11
10	1.72 ± 0.20
20	1.65 ± 0.13
40	1.11 ± 0.12

Table VII.   Effect of Fruit Acids on the Rate of Degradation of Sorbic Acid in Aqueous Solutions at 37 ± 1 °C

additive	pH	rate constant, $K_{obsd} \times 10^3$, h^{-1}
none	3.0	2.2 ± 0.14
malic acid	2.3	2.3 ± 0.16
maleic acid	1.7	2.8 ± 0.18
oxalic acid	1.5	2.5 ± 0.19
tartaric acid	2.2	2.9 ± 0.21
fumaric acid	2.2	3.3 ± 0.20
lactic acid	2.5	3.1 ± 0.14
citric acid	2.2	2.1 ± 0.14

in the present study may also be due to the decrease in solubility of oxygen which in turn will determine its availability in the reaction system.

Effect of fruit acids on the stability of SA is shown in Table VII. While citric and malic acid did not have a significant effect, all other acids exhibited a prooxidant action in SA degradation. The prooxidant action of fruit acids was, however, not related to the pH of the reaction systems. It is most likely that the overall effect of anion is more important than the pH alone. Earlier, Arya (1980) has observed that anions play an important role in the SA degradation. While chlorides of Na$^+$ and K$^+$ had a protective action, sulfates and phosphates of Na$^+$, K$^+$, and NH$_4^+$ exhibited a strong prooxidant action.

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