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Studies on identification of white specks in cured aonla (*Emblica officinalis* Gaertn.) fruits

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Aonla (*Emblica officinalis* Gaertn.), an Indian vitamin C-rich fruit, has great potential for pickling but the development of white specks during curing and pickling is a major hindrance. Studies to evaluate the effects of various pre-treatments on the development of white specks were carried out. The extent of white specks was less in aonla fruit segments preserved in steeping solution containing 10% salt and 0.04% KMS than in those preserved by dry, salting with 10% salt and 0.02% KMS during one month of storage. The fruits which developed white specks were poor in texture and brownish in colour. These white specks were isolated and extracted with water. The white specks thus obtained were purified as white solid matter. This was insoluble in water and other common organic solvents but soluble in alkali solutions. The IR and 'H NMR spectra and mp confirmed that the white solid matter isolated and purified from white specks of preserved fruits was mucic acid (D-galactaric acid). Its mineral analysis indicated the formation of some unknown complex of this compound with calcium and potassium. © 1998 Published by Elsevier Science Ltd. All rights reserved

INTRODUCTION

Aonla (*Emblica officinalis* Gaertn. Syn. *Phyllanthus emblica* L.), also known as Indian gooseberry, occupies an important position among arid zone minor fruits. This fruit is well known for its nutritional qualities (rich in ascorbic acid and tannins) and pharmaceutical properties. But raw fruits, being highly acidic and astringent in taste, are unacceptable to consumers. Therefore, they are generally processed to sugar-rich products such as preserves, candies, etc. (Kalra, 1988) and utilised for preparation of some pharmaceutical products (Sethi and Anand, 1982). An alternative is to process the nutritious fruit into a pickle, but the development of white specks on the surface and interior of the fruit is a major hindrance. The fruit, on development of white specks, become very poor in appearance and mushy in texture. Such pickles are immediately rejected by consumers which leads to heavy economic losses. Because of its nutritional and medicinal properties, the chemistry of aonla fruit has been studied in depth (Kalra, 1988). Pillay and Iyer (1958) reported a phenolic compound, emblicol, ($C_{20}H_{30}(OCH_3)_6$, mp 191–194°C), ellagic acid and other products in dried aonla fruit. Mucic acid (D-galactaric acid, $C_6H_{10}O_8$) was isolated and purified from dried ripe fruit by Soman and Pillay (1962) (having mp 208–210°C). In addition, mucic acid has been detected in putrefied blood, marine algae, grape vine shoots, Ceylon olive, ripe peaches and pears. However, no information is available on the development of white specks in steeped aonla fruit. Therefore, the present studies were undertaken to find the cause of white specks in cured aonla fruits and their pickle.

MATERIALS AND METHODS

Materials

The aonla fruits of Chakaiya and Desi varieties and other ingredients were obtained from the local market. All the reagents were of analytical grade.

Methods

The fruit were washed and segments of fruit were preserved with the following pre-treatments:

PT1: dry salting of raw segments with 10% salt and 0.02% potassium metabisulphite (KMS);

PT2: dry salting of steam blanched segments with 10% salt and 0.02% potassium metabisulphite (KMS);

PT3: steeping of raw segments in 10% salt and 0.04% KMS solution (1:1 ratio).

Physico-chemical analysis

Various physico-chemical parameters like texture, moisture, ascorbic acid, tannins, salt, pH, etc., were carried out as per standard methods (Ranganna, 1986). The white specks were isolated from the pretreated fruit. and white solid matter was extracted from these white specks with water. The white solid matter can then be dried in an oven at $55 \pm 1°C$. The resultant white solid matter (10 g) was treated with 15 ml of sodium hydroxide (5%), adjusted to pH 8.0 and purified further by the method of Pillay and Iyer (1958). The solubility was checked by dissolving a small quantity of matter in different organic and inorganic solvents and alkali solutions. The melting point was recorded in a capillary tube, using a melting point apparatus. The acetyl derivative was formed by refluxing a small quantity of white solid matter (200 mg) in a round bottom flask (500 ml) with acetic anhydride AR (100 ml) and benzene (100 ml) at 100°C for 4 h. The IR spectra of white solid matter and its acetyl derivative were recorded as KBr pellets on a Perkin–Elmer Model 405, Grating IR Spectrophotometer. ^{1}H NMR spectra were obtained on a Varian 60 MHz (model EM 360 L) instrument by using solvent CCl_4 containing TMS as an internal standard.

RESULTS AND DISCUSSION

Visual examination showed that a steeping solution containing 10% salt and 0.04% KMS was better in controlling the development of white specks than other pre-treatments like dry salting with or without steam-blanching (Fig. 4). The retention of texture and other chemical constituents, such as moisture, ascorbic acid, tannins, etc., were also higher in the fruit segments preserved by steeping method (Table 1). The fruits preserved by dry salting had maximum white specks as well as browning and softening. The white solid matter extracted (Fig. 3) and purified from white specks was insoluble in most of the organic solvents and mineral acids at ordinary temperature as well as on heating to boiling. It was partially soluble in pyridine showing a precipitated residue. However, this matter was found sparingly soluble in water and completely soluble in alkaline solutions of NaOH (4%), $NaHCO_3$ (1%) and Na_2CO_3 (1%). Powdered matter gave a turbid white suspension in water, whereas it gave a brownish colour solution in alkali. The suspension of white solid matter in distilled water had an acidic pH (pH 2.75) and it gave effervescence on addition of Na_2CO_3. These reactions clearly indicated the presence of acid in the white solid matter. The melting point of 208–209°C clearly matched that of mucic acid (D-galactaric acid, mp 208–210°C) as reported earlier by Soman and Pillay (1962). The infra red (IR) absorption spectrum of white solid matter and acetyl derivative (Figs 1 and 2) showed a prominent

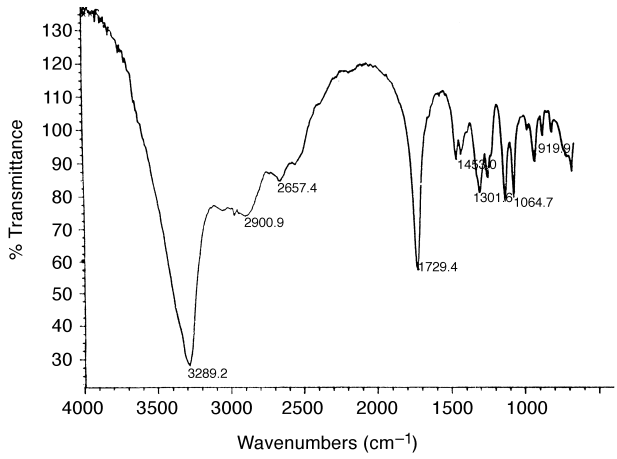

Fig. 1. IR spectra of white solid matter.

Table 1. Changes in physico-chemical composition of pretreated fruit segments during one month of storage

Variety	Pre-treatment	Chemical parameters (dry weight basis)					
		Texture (Newton)	Moisture (%)	Ascorbic acid (mg 100 g^{-1})	Tannins (% tannic acid)	pH	Salt (%)
Chakayia							
	Initial	9.65	87.17	4,491	24.8	2.82	
	PT1	3.74	74.85	836 (18.60)	313 (6.96)	2.66	48.2
	PT2	3.48	74.41	536 (11.92)	161 (3.60)	2.93	47.2
	PT3	9.64	84.7	1124 (25.03)	316 (7.04)	3.22	24.1
	Mean	5.63	77.99	832 (18.52)	264 (5.87)	2.94	39.8
Desi							
	Initial	10.89	89.8	3915	22.0	2.86	
	PT1	3.61	73.16	955 (25.38)	9.04 (41.13)	2.8	42.5
	PT2	1.43	76.4	652 (16.72)	8.87 (40.35)	2.8	38.5
	PT3	9.98	80.42	1844 (41.06)	6.33 (28.80)	3.38	17.4
	Mean	5.01	76.66	1151 (29.40)	8.08 (36.78)	2.99	32.8
CD (0.05)							
Variety		NS	0.28	8.76	0.73	NS	4.7
Pre-treatment		0.4	0.35	10.7	0.89	0.31	5.76
Variety X Pre-treatment		NS	0.49	15.2	NS	NS	NS

The values in parentheses are % retentions.
NS = Not significant.

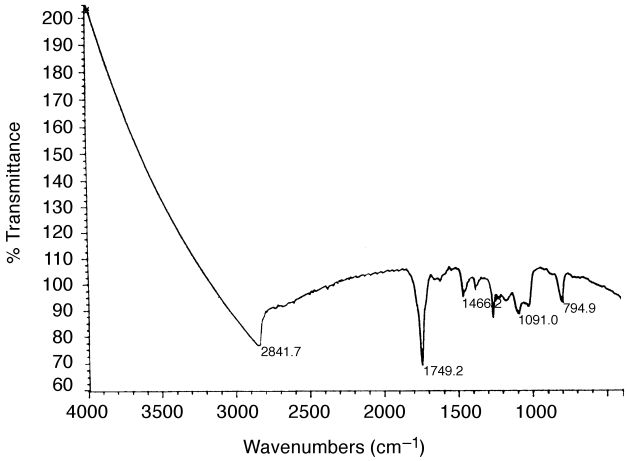

Fig. 2. IR spectra of acetyl derivative of white solid matter.

Table 2. The effect of different minerals on formation of white specks

Mineral (ppm dwb)	Fresh fruit	White solid matter	
		Crude	Purified
Calcium	1100 (168)	2750	110
Sodium	1250 (191)	2000	1750
Potassium	16 000 (2438)	500	Nil

Figures in parentheses are on fresh weight basis; dwb = dry weight basis.

Fig. 3. Crupe white solid matter (specks) extracted from steeped aonla fruits.

band at 3289.2 cm^{-1}, whereas this band was absent in the acetyl derivative. The absence of IR band stretching at 3289.2 cm^{-1}, and a prominent peak at 2841.7 cm^{-1}, indicated the formation of an acetyl derivative at a very high temperature. The formation of acetyl derivative was also confirmed by a singlet peak at δ 2.03 in the

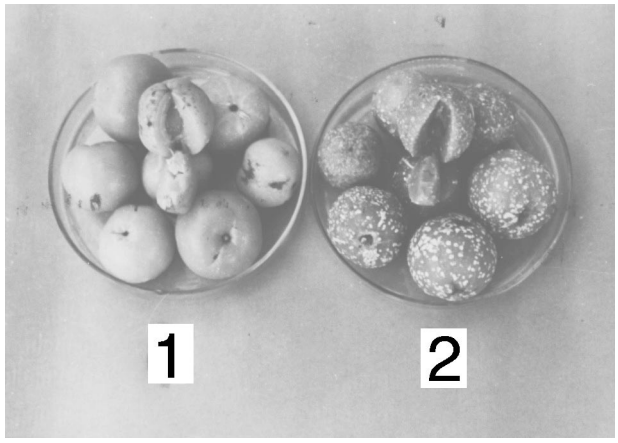

Fig. 4. 1. Steeping in 10% salt and 0.04% KMS solution. 2. Dry salting in 10% salt + 0.02% KMS.

^{1}H NMR spectrum taken in CCl_4, integrating for 12 protons. The IR spectrum (as KBr pellets of purified white solid matter) was fully superimposible on the IR-spectrum of mucic acid as reported earlier (Tipson and Clapp, 1953) which clearly indicated that the compound under examination might be a mucic acid derivative. Thus the qualitative tests, IR and ^{1}H NMR spectra and mp confirmed that the white solid matter isolated from white specks of cured aonla fruits was mucic acid (D-galactaric acid) having molecular formula $C_6H_{10}O_8$. During curing of aonla fruit, this natural fruit constituent, accumulated on the surface and interior of the fruits. The process of development of white specks was induced by addition of calcium to the brine solution. The role of sodium and calcium in the formation of white specks was confirmed by the retention of these minerals during the purification process (Table 2).

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