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Volatile Flavor Components of Sapodilla Fruit (*Achras sapota* L.)

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An essence of fresh sapodilla fruit was obtained by well-established procedures, and it possessed the characteristic aroma of the fruit. It was analyzed by GC–MS with both EI and CI techniques. The fruit produced a relatively small quantity of aroma volatiles (in total about 5 μg/kg of fresh fruit), less than that obtained from most similar fruits, and this partly explains its delicate flavor. A group of "benzyl-related" compounds comprised over 45% of the essence and included a series of five alkyl benzoates. Methyl benzoate and methyl salicylate were both described as having sapodilla fruit aroma on odor evaluation of separated components at an odor port at the exit of the GC column. Ethyl benzoate and propiophenone had related aroma characteristics.

Sapodilla (*Achras sapota* L.) is a medium-sized tree native to Central America, but it is also grown elsewhere in the tropics. It is best known as the source of chicle gum (the coagulated latex) which is the basis for chewing gum manufacture. However, it also produces an edible fruit possessing a characteristic and most attractive delicate flavor. The fruit is very sweet and best consumed raw, but fully ripe. When underripe, it has a rather unappealing alcoholic aftertaste. Although perhaps not well-known elsewhere, sapodilla is considered one of the best fruits of the American tropics. It is grown on a commercial scale in some Central American countries, but produce is marketed fresh and currently the fruit is not processed in any way, although the juice provides a most refreshing drink which might have commercial potential.

To data there has been no study of the nature of the volatile aroma components contributing to the desirable flavor of sapodidilla fruit, and this paper describes the first such survey. However, Oliveros-Belardo et al. (1971) extracted the essential oil from the whole fruit (i.e., pulp with peel intact) of Philippine sapodilla and described its odor as spicy, aromatic and eugenol-like. This odor was reported to be remote from that of the fresh fruit itself; no chemical analysis of the essential oil was undertaken. Nilo Rivas and de Martos (1979) have described some physical and chemical properties of three selections of sapodilla from the state of Zulia in Venezuela, but flavor compounds and flavor properties were not considered.

EXPERIMENTAL SECTION

Fresh sapodilla fruits were transported by air from Venezuela such that they could be analyzed almost immediately on arrival in their ripe state.

Sample Preparation. Fruit pulp (983 g) was mixed with water (400 mL) and extracted for 3 h in a Likens and Nickerson (1964) apparatus as modified by MacLeod and Cave (1975) by using triply distilled 2-methylbutane (25 mL) as the solvent. At the end of this time the residue did not possess any appreciable aroma. The extract was concentrated to 1.0 mL as previously described (MacLeod and Cave, 1975), and the resultant essence possessed a strong aroma, characteristic of the fresh fruit.

Gas Chromatography. Essences were examined by gas chromatography with a Pye-Unicam 204 instrument equipped with heated FID. An 18 ft × 4 mm i.d. glass column was used, packed with 10% PEG 20M coated on 100–120 BSS mesh acid-washed Diatomite C. Nitrogen carrier gas was used (60 mL/min), and the temperature program was 60 °C for 5 min, followed by an increase of 12 °C/min to 180 °C for the remainder of the run. Detector and injection temperatures were 250 °C.

Gas Chromatography–Mass Spectrometry. Components in the essence were identified as far as possible by GC–MS with a Kratos MS 25 instrument linked on-line to a Kratos DS 50 data processing system. The same GC conditions as described above were employed but using helium as the carrier gas and a lower flow rate (30 mL/min). A single-stage, all-glass jet separator was used at 250 °C. Significant operating parameters of the mass spectrometer during electron impact ionization work were as follows: ionization voltage, 70 eV; ionization current, 100 μA; source temperature, 230 °C; accelerating voltage, 1.5 kV; resolution, 900; scan speed, 1 s/decade (repetitive throughout the run). Identical conditions were employed during chemical ionization mass spectrometry except for the following: reagent gas, methane; ionization potential, 100–110 eV; emission current, 5 mA.

Quantitative Assessment. Samples were prepared in such a manner that a known aliquot of the fruit sample was analyzed. Quantitative data were then derived both from the trace obtained from the TIC monitor during GC–MS and from the FID trace during routine GC. Known amounts of a selection of identified compounds (*trans*-hex-2-enal, benzaldehyde, methyl benzoate, and methyl salicylate) were injected under the same analytical conditions in order to enable calculation of absolute amounts of components in the essence.

Odor Assessment. Aromas of the separated components of the essence were assessed at an odor port following GC by using a Pye-Unicam 104 instrument. An outlet splitter set at 10:1 diverted the major fraction of the eluent through a heated line to the outside of the GC oven for aroma assessment by three subjects, two of whom were familiar with sapodilla fruit flavor.

RESULTS AND DISCUSSION

Valid aroma concentrates of fresh sapodilla fruit were obtained by using previously described methods (MacLeod and Pieris, 1981b), and constituents were identified as far as possible by GC–MS with both electron impact ionization and chemical ionization techniques.

Table I lists the volatile flavor components of fresh sapodilla fruit, together with GC retention data, quantitative data, and odor qualities of the various GC peaks. There were only two detectable impurities originating from the isopentane solvent (determined on a blank run following concentration of the solvent), and these have not been included in the table. In all instances where positive identities are given in Table I, mass spectra agreed with

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Table I. Volatile Flavor Components of Sapodilla Fruit (*Achras sapota* L.)

peak no.	component	t_R, min	Kovats index (lit.)	positive identn by MS	% rel abund.	μg/kg of fruit	odor quality
1	cyclohexane	2.8	765	✓	0.3	0.02	
2	branched C_7 hydrocarbon	3.3			0.2	0.01	
3	branched C_8 hydrocarbon	4.0			tr[a]	tr	
4	methylcyclohexane plus branched C_8 hydrocarbon	4.7		✓	12.4	0.64	
5	octane	4.9	800	✓	4.3	0.22	slightly sweet, fruity
6	a dimethylcyclohexane	5.2		✓	0.7	0.04	sweet, slightly roasted
7	a dimethylcyclohexane	5.6		✓	0.4	0.02	fruity, apricot
8	a methylcyclohexene	5.9		✓	tr	tr	
9	unknown	6.6			0.1	0.01	buttery
10	ethylcyclohexane	6.9		✓	0.3	0.02	buttery
11	ethanol plus 3-methylbutanal	7.4	900 937	✓ ✓	0.6	0.03	green, buttery, sweet
12	benzene	8.0	970	✓	tr	tr	
13	butanedione	8.8	963	✓	<0.1	<0.01	diacetyl-like
14	2-methylbutan-2-ol	9.3	987	✓	0.3	0.02	
15	chloroform	10.0		✓	0.4	0.02	fruity
16	toluene	10.3	1055	✓	6.4	0.35	sweet, caramel
17	dimethyl disulfide plus hexanal	11.5	1081 1084	✓ ✓	4.3	0.22	green grass, hexanal, slightly musty
18	butan-1-ol	12.2	1113	✓	0.6	0.03	sweet, sickly
19	*m*- and/or *p*-xylene	12.9	1145	✓	0.5	0.03	cold meat, fat
20	car-3-ene	13.2	1165	✓	1.5	0.08	fruity, estery (20 and 21)
21	3-methylbutan-1-ol	13.4	1184	✓	1.6	0.08	
22	*o*-xylene	13.8	1191	✓	2.5	0.13	cold meat, fat
23	*trans*-hex-2-enal	14.2	1207	✓	4.7	0.24	green, hexenal
24	hexyl acetate	14.9	1307	✓	0.3	0.02	fruity, peach
25	styrene	15.3		✓	0.1	0.01	buttery
26	(?)3-hydroxybutan-2-one	15.5			0.4	0.02	slightly musty
27	a monoterpene	15.8			tr	tr	
28	hexan-1-ol	16.0	1316	✓	3.2	0.17	fruity
29	unknown	16.4			tr	tr	
30	anisole	16.6	1327	✓	0.1	0.01	stale green
31	isopropylbenzene	17.0		✓	tr	tr	
32	hydrocarbon	17.3			<0.1	<0.01	fruity
33	dimethyl trisulfide	17.7	1400	✓	tr	tr	unpleasant, sulfurous
34	*cis*-linalool oxide	18.0	1423	✓	tr	tr	
35	furfural	18.2	1449	✓	tr	tr	cooked, roast meat
36	*trans*-linalool oxide	18.7	1451	✓	0.3	0.02	fatty, oily
37	acetylfuran	19.4	1491	✓	0.2	0.01	floral, fragrant
38	benzaldehyde	20.7	1502	✓	22.3	1.15	almonds, benzaldehyde-like
39	branched C_{16} hydrocarbon	21.8			0.1	0.01	green
40	unknown	22.7			<0.1	<0.01	sweet, fruity
41	methyl benzoate	23.2	1600	✓	14.3	0.74	medicinal, phenolic, sapodilla
42	caryophyllene	24.0	1618	✓	0.2	0.01	sweet, fragrant, wallflowers
43	ethyl benzoate	24.5	1647	✓	3.9	0.20	medicinal, fruity
44	heptadecane	25.4	1700	✓	0.2	0.01	stale, slightly green
45	propiophenone	26.9		✓	0.1	0.01	medicinal, phenolic
46	benzyl methyl ketone	28.7		✓	1.9	0.10	hay, nutty, oily
47	methyl salicylate	29.2	1754	✓	1.2	0.06	medicinal, phenolic, sapodilla
48	octadecane	29.7	1800	✓	0.2	0.01	cereal, grainlike
49	benzyl alcohol	33.0	1822	✓	2.5	0.13	hay, cereal, slightly fruity
50	butyl benzoate plus benzyl 3-methylbutanoate	33.9	1841 1880	✓ ✓	0.5	0.03	sweet, hay, peach
51	unknown	35.1			tr	tr	
52	nonadecane	36.2	1900	✓	0.7	0.04	
53	pentyl benzoate	39.1	1940	✓	tr	tr	peach, nectarine
54	hydrocarbon	43.8			tr	tr	
55	hydrocarbon	44.2			tr	tr	
56	methyleugenol	45.5		✓	0.5	0.03	fruity, hay
57	3-phenylpropan-1-ol	47.4	1993	✓	3.8	0.20	peach, nectarine
58	methyl anisate	50.0	2071	✓	0.6	0.03	sweet, sickly, honey
59	hexyl benzoate	53.0	2066	✓	0.2	0.01	fruity, sweet, cereal-like
60	hydrocarbon	55.0			tr	tr	
61	hydrocarbon	58.0			tr	tr	

[a] tr = trace.

those in the literature, within instrumental variability. All spectra have been published previously, so none need be reported here. Literature [e.g., Andersen and Falcone (1969) and Jennings and Shibamoto (1981)] Kováts retention indices of some important components are also included in the table. These values were determined on the same GC phase as that employed in this project, and they serve as useful, but limited, confirmation of identity. Where no odor quality is given in the table, this was either due to none being detected or due to a minor peak being incompletely resolved from an adjacent larger peak such that no distinctively different odor could be perceived.

In total, just over 5 μg of aroma components was obtained per kg of fresh fruit. This is a very low concentration, and although it does not take account of varying odor potencies of different compounds, it does partly explain the delicate flavor of sapodilla fruit. In our recent analyses of other tropical fruits using similar techniques, with one exception greater amounts of volatiles have always been obtained. For example, guava (*Psidium guajava*) produced just over 200 μg/kg (MacLeod and de Troconis, 1981), soursop (*Annona muricata*) provided about 1.2 mg/kg (MacLeod and Pieris, 1981b), and the strongly flavored wood apple (*Feronia limonia*) gave about 80 mg/kg (MacLeod and Pieris, 1981a). Thus wood apple liberated about 16 000 times the concentration of aroma volatiles compared with sapodilla fruit. Mangosteen (*Garcinia mangostana*), which also has a very delicate flavor, was found to produce slightly lesser amounts of volatiles than sapodilla, at about 3 μg/kg (MacLeod and Pieris, 1982).

Table I shows that the sapodilla fruit essence contained 65 main components, of which 47 (comprising about 98% of the sample) were positively identified, with a further 14 (~1.8%) partially or tentatively characterized. The compounds identified cover a range of compound types, including hydrocarbons (aliphatic, alicyclic, and aromatic), alcohols, aldehydes, and ketones (aliphatic and aromatic in all cases), esters, and mono- and sesquiterpenes. Important specific compounds on the basis of concentration in the essence and/or odor qualities include 3-methylbutan-1-ol, *trans*-hex-2-enal, hexan-1-ol, benzaldehyde, methyl benzoate, ethyl benzoate, methyl salicylate, and car-3-ene.

The fruit produced an interesting series of "benzyl-related" compounds, conceivable of some common origin. Thus, in addition to benzaldehyde, relatively large amounts of benzyl alcohol and benzyl methyl ketone were detected. Also, a series of benzoates from methyl to hexyl was identified, with the lower members being produced in greater amounts. However, propyl benzoate was missing from the series. From its Kováts index (1745) it would be expected to elute from the GC at about the same retention time as methyl salicylate (peak 47), but although careful searches were made in this region of the GC–MS runs, no indication of its presence could be detected in any mass spectra. The benzyl-related compounds comprised just over 45% of the sapodilla fruit essence, and also taking into account their aroma properties, these compounds must contribute especially to the characteristic flavor of the fresh fruit. However, all these benzyl components are widespread among aroma volatiles, and the benzoates, for example, have importance in many fruits, including cherry, banana, peach, pineapple, grape, and citrus fruits in general (van Straten and de Vrijer, 1973).

The major terpene in the sapodilla sample was the monoterpene hydrocarbon car-3-ene (1.5%), and this is worthy of brief comment, since it is not one of the more common terpene aroma volatiles. It has, however, been previously detected in various spices and in tomato, currant, passion fruit, and citrus fruits in general (van Straten and de Vrijer, 1973). In this project there was no doubt concerning its identification both on the basis of its retention behavior (see Table I) and on the basis of the production of a good mass spectrum which agreed perfectly with that quoted in the literature (Ryhage and von Sydow, 1963).

On assessment at an odor port during GC, two peaks were described as possessing significant sapodilla fruit character. These peaks were due to methyl benzoate (peak 41, 14.3% of the total volatiles of the sample) and methyl salicylate (peak 47, 1.2%). These compounds could therefore be considered to be particularly important contributors to characteristic sapodilla fruit flavor. However, on the basis of their associated odor descriptions ("medicinal" and "phenolic"), it is possible that ethyl benzoate (peak 43) and propiophenone (peak 45) might also contribute to characteristic sapodilla flavor, although neither GC peak due to these compounds was described specifically as possessing sapodilla aroma. A mixture, at the determined concentrations (Table I) in an inert solvent (2-methylbutane), of these four compounds, together with benzaldehyde, hexan-1-ol, and *trans*-hex-2-enal, did indeed provide an aroma somewhat reminiscent of fresh sapodilla fruit, but it was not, as would be expected, entirely characteristic. However, it was sufficiently similar to the fresh fruit for it to be suggested that these compounds are major contributors to sapodilla fruit flavor.

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