

Volatile Components of Papaya (*Carica papaya* L.) with Particular Reference to Glucosinolate Products

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The aroma volatiles of fresh papaya fruit from Sri Lanka were extracted and concentrated to a valid essence by using well-established techniques. Analysis by GC and GC-MS showed at least 50 components (total about 97 $\mu\text{g}/\text{kg}$ of fruit), of which 18 were identified for the first time as papaya volatiles. Esters afforded the most abundant group of compounds, with methyl butanoate being the major constituent (about 48% w/w of the sample). It is suggested that this component is the one mainly responsible for the pronounced sweaty odor quality of some papaya fruit. Many significant differences were observed between these results and those previously obtained for Hawaiian papaya. Products of benzylglucosinolate degradation were identified in relatively large amounts in both fruit and seeds of papaya, but no benzyl thiocyanate could be detected despite high-sensitivity searches by means of multipeak monitoring GC-MS. Similarly, no methylglucosinolate degradation products could be detected, and it was not possible to confirm previous identification of methyl thiocyanate.

Papaya (*Carica papaya* L.) also commonly known as "pawpaw", is a native of tropical America, but it is now widely planted throughout the tropics. In recent years it has become increasingly important as a commercial fresh fruit crop, particularly in the United States where it is mainly grown in Hawaii. However, the fruit has also become popular in Europe and is imported from various growing regions throughout the world. The fresh fruit can be successfully preserved and canned products are readily available.

Despite the obvious importance of papaya fruit and its large market, there have been relatively few studies of the volatile components that contribute to its desirable flavor. Probably the first such study was by Katague and Kirch (1965), but the most comprehensive and detailed investigation to date was by Flath and Forrey (1977), who identified a total of 106 volatile constituents from Hawaiian papaya. However, it has been shown with another tropical fruit, mango, that the composition of volatiles can vary considerably depending on the cultivar and/or region of production of the fruit (MacLeod and de Troconis, 1982c; MacLeod and Pieris, 1983). In addition, fresh (and canned) papaya as obtained in England has a pronounced pervading sweaty note to the aroma, which would be difficult to explain on the basis of the constituents identified by Flath and Forrey (1977). It was decided, therefore, to reexamine the volatile components of papaya and to study in particular the fruit from Sri Lanka, which has not been analyzed before. A specific objective was to attempt to detect any component(s) that could be responsible for the sweaty aroma.

Papaya is also interesting in that it contains benzylglucosinolate, and hence produces, by enzyme action, benzyl isothiocyanate among its volatiles. Glucosinolates are thioglucosides mainly located in the botanical family Cruciferae, and although isolated occurrence outside this family is well documented, it is rare. One of the best known examples of a non-Cruciferae, glucosinolate-containing species is *Carica papaya*. This was first demonstrated many years ago (Ettlinger and Hodgkins, 1956) but has since been frequently confirmed (Gmelin and Kjaer, 1970; Tang, 1970, 1971; Tang and Syed, 1972). Benzyl-

glucosinolate has also been detected in other *Carica* species as well as *C. papaya* (Gmelin and Kjaer, 1970).

In their study of papaya fruit, Flath and Forrey (1977) further confirmed the presence of benzylglucosinolate, in that they detected relatively large amounts of both benzyl isothiocyanate and phenylacetone nitrile (another product of benzylglucosinolate degradation) among the volatile components. In addition, they identified traces of methyl thiocyanate, and it might seem possible that this could also have glucosinolate origin. However, this would be somewhat unexpected since, of the approximately 90 known glucosinolates, only three have so far been shown capable of undergoing degradation to yield a thiocyanate, and methylglucosinolate is not one of the three. Furthermore, it would then be additionally surprising that benzyl thiocyanate was not also detected in papaya volatiles, since benzylglucosinolate is one of the three known thiocyanate-forming glucosinolates. Flath and Forrey (1977) proved their component to be methyl thiocyanate and not the isothiocyanate, and it is possible that the thiocyanate could have non-glucosinolate origin, but it was decided in this work also to examine papaya specifically for these particular glucosinolate products. Thus seeds (which are richer in glucosinolates) were investigated as well as the fruit, and specific searches were made in all samples for acetonitrile, methyl isothiocyanate, methyl thiocyanate, and benzyl thiocyanate.

EXPERIMENTAL SECTION

Sample Preparation. Fruits were peeled and the seeds carefully removed. Pulp (840 g) was mixed with water (200 mL) and extracted for 3 h in a Likens and Nickerson (1964) apparatus as modified by MacLeod and Cave (1975) using purified pentane (15 mL) as the solvent. At the end of this time the residue did not possess any detectable aroma. The extract was concentrated to 1.0 mL as previously described (MacLeod and Cave, 1975).

Gas Chromatography. Essences were examined by gas chromatography using Pye-Unicam 204 and Philips PU 4500 instruments, both equipped with a heated FID. Most work was done with 25 m \times 0.2 mm i.d. fused silica capillary columns containing PEG 20M or OV-101 or BP20 bonded phase (equivalent to PEG 20M) or BP1 bonded phase (equivalent to OV-101). Hydrogen carrier gas was used (0.8 mL/min) and the temperature program was 65 $^{\circ}\text{C}$ for 3 min, followed by an increase of 12 $^{\circ}\text{C}/\text{min}$ to 180 $^{\circ}\text{C}$ for the remainder of the run. Detector and injection point heaters were 275 and 250 $^{\circ}\text{C}$, respectively, and typically 0.1 or 1.0 μL was injected at a 25:1 split. Other

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columns used were 5.5 m \times 4 mm i.d. glass packed with either 10% PEG 20M or 3% OV-101 coated on 100–120 BSS mesh acid-washed Diatomite C, with nitrogen (30 mL/min) as the carrier gas and the same temperature program.

Gas Chromatography–Mass Spectrometry. Components in the essence were identified as far as possible by GC–MS using a Kratos MS 25 instrument linked online to a Kratos DS 50S data processing system and equipped with a computer-controlled multiplex monitoring (MPM) unit. The same GC conditions as described above were employed but using helium as the carrier gas. 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 μ A; source temperature, 225 °C; accelerating voltage, 1.33 kV; resolution, 1500; scan speed, 1 s/decade (repetitive throughout run). Identical conditions were employed during chemical ionization mass spectrometry except for the following: reagent gas, isobutane; 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 (methyl butanoate, toluene, *cis*- β -ocimene, benzaldehyde, phenylacetonitrile, and benzyl isothiocyanate) were injected under the same analytical conditions in order to enable assessment 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 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 two subjects, both of whom were familiar with papaya fruit flavor.

Analysis of Papaya Seeds for Glucosinolate Products. Seeds (120 g) were pulped and mixed with water (250 mL), and a crude preparation of mustard thioglucoside glucosyltransferase [100 mg, prepared by the method of Schwimmer (1961)] was added together with ascorbic acid (1 g), which is a known cofactor for optimum thioglucosidase activity. Autolysis was allowed to proceed in a stoppered flask, with shaking, for 1.5 h to ensure complete glucosinolate degradation. Autolysates were then either extracted with isopentane (15 mL) in the Likens and Nickerson apparatus as already described for the fruit or further processed as follows. The seed residue was removed by centrifugation and the aqueous layer extracted with dichloromethane (2 \times 30 mL). Following centrifugation, the organic layer was separated, dried (Na_2SO_4), and carefully reduced in volume to less than 5 mL by using a rotary evaporator without the application of heat. Samples from both procedures were analyzed as such and also after further concentration by low-temperature-high-vacuum distillation (MacLeod and Cave, 1975). Analysis involved routine GC–MS, high-sensitivity MPM GC–MS, and high-sensitivity GC alone, with comparison of retention times of peaks with those of authentic standards chromatographed under identical conditions.

RESULTS AND DISCUSSION

Fresh, ripe papaya fruits were obtained from local markets in Colombo, Sri Lanka. Valid aroma extracts were prepared the same day by using well-established proce-

dures that have been previously reported (MacLeod and de Troconis, 1982a). The extracts were concentrated by high-vacuum-low-temperature distillation, and the resultant essences were found, on appropriate redilution, to possess characteristic papaya aroma. The concentrates were analyzed by GC and GC–MS (using both electron impact and chemical ionization mass spectrometry), and results are given in Table I. A number of GC columns were employed, including packed columns and fused silica capillary columns (both with PEG 20M or OV-101 stationary phases) and bonded-phase fused silica capillary columns containing either a BP1 (equivalent to OV-101) or BP20 (equivalent to PEG 20M) stationary phase. The retention data given in Table I were obtained by using a 25-m fused silica column coated with BP20. Kováts retention indices (Jennings and Shibamoto, 1980) of most components (on PEG 20M) are also included in the table, and they confirm the general elution sequence. The qualitative data in the table were mainly obtained by using both packed columns and both bonded-phase fused silica columns; some components were best identified by GC–MS using one particular phase and/or type of column. In all instances where positive identities are given, the mass spectra obtained on GC–MS agreed with those in the literature [e.g., Jennings and Shibamoto (1980)].

The quantitative data in Table I show that in total about 97 μ g of aroma components was obtained per kg of fresh fruit (excluding skin and seeds). In comparison with other tropical fruits analyzed recently by us using broadly the same procedures, this is an average level. Thus, for example, soursop yielded about 1200 μ g/kg aroma components (MacLeod and Pieris, 1981), guava about 200 μ g/kg (MacLeod and de Troconis, 1982b), mango about 60 μ g/kg (MacLeod and de Troconis, 1982c), and mangosteen about 3 μ g/kg (MacLeod and Pieris, 1982).

Table I shows that 50 volatile components were detected in Sri Lankan papaya essence. Of these, 37 (comprising about 99.5% w/w of the volatiles) were positively identified and one, present in only trace amount, was partially characterized. Thus, the unidentified constituents comprised only about 0.5% w/w of the sample. Of the fully identified components, 18 are here reported as papaya volatiles for the first time. A fairly wide range of different types of compounds was detected, including hydrocarbons, alcohols, aldehydes, ketones, acids, esters, lactones, etc., but only five terpenoids were recognized, including four linalool-related compounds. Most tropical fruits recently analyzed by us have contained large numbers of terpenes, usually providing the major class of volatiles, but occasionally esters have contributed the main group of volatiles, and soursop yielded 80% of its volatiles as esters (MacLeod and Pieris, 1981). The volatiles of Sri Lankan papaya were also dominated by esters (15, about 53% w/w of the sample), with the major representatives (51% w/w of the sample) being a complete range of six methyl esters of even-carbon-numbered carboxylic acids from butanoate to tetradecanoate inclusive. For Hawaiian papaya (Flath and Forrey, 1977), terpenoids did provide the most abundant group of volatiles, but this is a little misleading in that one compound alone (linalool) constituted about 68% of the sample, with linalool oxides providing another 13%. Although a large number of esters were identified in papaya by Flath and Forrey (1977), together they comprised less than 1% of the sample. It is immediately obvious, therefore, that there are major differences between the main groups of volatile components of papaya from Hawaii and from Sri Lanka, which would be expected to provide quite different flavor characteristics to the fruits.

Table I. Volatile Constituents of Papaya (*C. papaya* L.)

peak no.	component	new identification	t_R , min	Kováts index (lit.)	% rel abund	$\mu\text{g}/\text{kg}$	odor quality
1	methylcyclohexane		0.5	800	4.7	4.5	
2	unknown		1.0		0.2	0.2	roasted cereal
3	unknown		1.2		tr ^a	tr	
4	2-methylbutanal	✓	1.4		6.2	6.0	stale green, fecal
5	butanedione	✓	1.6	963	tr	tr	diacetyl
6	methyl butanoate		1.8	975	48.3	46.7	rancid butter, sweaty
7	unknown		2.3		tr	tr	buttery
8	toluene		2.7	1055	4.8	4.6	
9	unknown		3.6		0.1	0.1	
10	methyl but-2-enoate		4.1	1100	0.3	0.3	
11	methyl hexanoate		5.9	1177	0.6	0.6	
12	pyridine	✓	6.0	1180	0.1	0.1	oily, fatty, pungent
13	<i>o</i> -xylene		6.1	1191	tr	tr	
14	unknown		7.2		0.1	0.1	
15	unknown		7.6		tr	tr	
16	<i>cis</i> - β -ocimene	✓	7.9	1228	0.4	0.4	mint
17	styrene	✓	8.0		0.1	0.1	
18	methyl hex-2-enoate	✓	9.0		0.1	0.1	
19	dimethylformamide	✓	9.5		0.1	0.1	musty, mouldy
20	octan-3-ol	✓	9.6		tr	tr	
21	methyl octanoate	✓	9.8	1378	0.2	0.2	floral, geranium
22	methyl (methylthio)acetate	✓	10.0		0.2	0.2	American currant
23	<i>cis</i> -linalool oxide (5-membered ring)		10.6	1423	7.3	7.1	pungent, urinary
24	<i>trans</i> -linalool oxide (5-membered ring)		10.8	1451	0.7	0.7	cold meat fat, stale
25	unknown		10.9		tr	tr	meat extract
26	linalool		11.0	1506	0.6	0.6	floral, fragrant, honeysuckle
27	benzaldehyde		11.1	1502	0.3	0.3	almonds
28	methyl furoate	✓	11.6	1561	0.1	0.1	
29	methyl decanoate		11.8	1581	0.8	0.8	floral, fragrant
30	a butanoate		11.9		tr	tr	
31	methyl benzoate		12.7	1600	0.2	0.2	fruity, estery, papaya
32	phenylacetaldehyde	✓	13.1	1646	0.8	0.8	floral, fragrant, roses geranium
33	unknown		13.2		tr	tr	floral
34	unknown		13.3		tr	tr	dandelions
35	<i>cis</i> -linalool oxide (6-membered ring)		13.5		1.1	1.1	citrus, medicinal
36	unknown		13.9		tr	tr	dandelions
37	unknown		14.3		tr	tr	
38	methyl nicotinate	✓	14.5	1779	0.5	0.5	slightly fruity, sickly
39	methyl dodecanoate	✓	14.6	1785	0.7	0.7	
40	hexanoic acid	✓	14.9		tr	tr	
41	benzyl alcohol		15.5	1822	0.2	0.2	
42	benzyl butanoate		16.5	1856	0.3	0.3	pleasant estery, fruity, floral, fragrant
43	2-phenylethanol		17.0	1859	0.2	0.2	lemon, geranium
44	phenylacetonitrile		18.4		17.7	17.1	pungent, almond, cereal, slightly musty
45	δ -octalactone		19.5	1929	0.1	0.1	cinnamon
46	methyl tetradecanoate	✓	19.8	1990	0.2	0.2	
47	octanoic acid	✓	21.0		tr	tr	
48	benzyl but-2-enoate	✓	21.7		0.1	0.1	fruity, estery
49	benzyl isothiocyanate		23.5		1.5	1.4	earthy, cress seeds
50	unknown		26.3		tr	tr	

^a tr = trace.

The most abundant compound in the Sri Lankan papaya volatiles was methyl butanoate (48.3%, 46.7 $\mu\text{g}/\text{kg}$), in contrast to the 68% of linalool obtained from Hawaiian papaya by Flath and Forrey (1977). Although linalool was also detected in Sri Lankan papaya, it was produced in a small amount (0.6%, 0.6 $\mu\text{g}/\text{kg}$). Three of the four possible linalool oxides were also identified [all were detected by Flath and Forrey (1977)], with the tetrahydrofuranyl *cis*-linalool oxide (7.3%, 7.1 $\mu\text{g}/\text{kg}$) being the major component of the three. Although the previous workers did no odor assessments in their study (Flath and Forrey, 1977), from our odor descriptions of methyl butanoate and linalool as determined at a GC odor port (see Table I), there was considerable difference between the odor qualities that, again, would be expected to cause appreciable flavor difference between papaya from Hawaii and Sri Lanka. The

perceived odor quality of methyl butanoate (Table I) suggests that this compound is mainly, if not exclusively, responsible for the characteristic sweaty note of some papaya fruit, as previously mentioned. However, it is possible that the relatively large amount of 2-methylbutanal (6.2%, 6.0 $\mu\text{g}/\text{kg}$) might also contribute somewhat to that odor. Very little methyl butanoate (0.06%) and no 2-methylbutanal were detected by Flath and Forrey (1977), and this implies that Hawaiian papaya should exhibit little or none of this particular sweaty odor quality.

Only one of the papaya volatiles was described as having any papaya quality on odor assessment at the GC odor port, and this was methyl benzoate. It is possible, therefore, that this compound might have some special importance to good papaya flavor. It was also detected, in a trace amount, by Flath and Forrey (1977).

The second most abundant constituent of Sri Lankan papaya volatiles was phenylacetone nitrile (17.7%, 17.1 $\mu\text{g}/\text{kg}$), a product of benzylglucosinolate degradation. Much lesser amounts of benzyl isothiocyanate were obtained (1.5%, 1.4 $\mu\text{g}/\text{kg}$), and this is the reverse of the relative distribution of these components as observed by Flath and Forrey (1977) (0.4% and 13.1%). Taking into account the strong and characteristic aroma of benzyl isothiocyanate, and to a lesser extent that of phenylacetone nitrile as well (see Table I), this difference could also have some effect on the relative flavors of the two types of papaya. The detailed mechanisms of glucosinolate degradation are not fully understood, so it is not particularly surprising that differing relative amounts of products are formed by the two types of fruit. In particular, nitrile formation is favored over isothiocyanate at lower pH, and it may simply be that Sri Lankan papaya is more acidic than Hawaiian papaya.

It can be seen from Table I that no other glucosinolate products were detected in Sri Lankan papaya fruit volatiles, apart from the two just mentioned. In particular, specific searches were made for methylglucosinolate products and for benzyl thiocyanate, by using the high-sensitivity MPM facility of the GC-MS system. However, it is well-known that the seeds of glucosinolate-containing species are invariably far richer in glucosinolates than any other parts of the plant. Thus, seeds of papaya were also analyzed but specifically for glucosinolate products. Conventional autolysis procedures were adopted, and exogenous thioglucosidase enzyme (ex mustard) was added to ensure, as far as possible, maximum degradation of glucosinolates. Extracts of autolysates were then examined for glucosinolate products as before but by employing in particular high-sensitivity MPM GC-MS. Large quantities of phenylacetone nitrile and benzyl isothiocyanate were readily detected and taken together indicated that papaya seeds contained about 0.56% w/w of benzylglucosinolate. This is in very good agreement with a previous analysis of papaya seeds (Chan et al., 1978), but the figure should also be compared with the percentage of benzylglucosinolate in papaya fruit, which can be estimated from the data in Table I to be about 4×10^{-6} %.

No benzyl thiocyanate could be detected in papaya seed autolysates. This is not necessarily surprising, since it has been adequately demonstrated in many previous studies that in natural systems benzylglucosinolate sometimes degrades to give thiocyanate but sometimes does not. For example, the thiocyanate is produced by the seeds of *Lepidium sativum* (cress) (Gil and MacLeod, 1980b) but not by the leaves (Gil and MacLeod, 1980a), and it has been suggested many times that some "thiocyanate-forming factor" is necessary in addition to thioglucosidase. Evidence has recently been gained for the presence of such a biological factor in *L. sativum* seeds (Hasapis and MacLeod, 1982). It would follow, therefore, that this factor is not present in papaya seeds, and this is further evidence against the previously identified methyl thiocyanate from papaya fruit (Flath and Forrey, 1977) being of glucosinolate origin. Furthermore, in this current work, no indication of the presence of methylglucosinolate could be

obtained, in that no acetonitrile, methyl isothiocyanate, or methyl thiocyanate could be detected in papaya seed autolysates, despite considerable attention to this aspect of the analysis. Therefore, the previous identification of traces of methyl thiocyanate in papaya fruit volatiles (Flath and Forrey, 1977) would appear to be yet another difference, albeit a minor one, between Hawaiian and Sri Lankan papaya, but it is unlikely that the thiocyanate was of glucosinolate origin.

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Registry No. Methylcyclohexane, 108-87-2; 2-methylbutanal, 96-17-3; butanedione, 431-03-8; methyl butanoate, 623-42-7; toluene, 108-88-3; methyl but-2-enoate, 18707-60-3; methyl hexanoate, 106-70-7; pyridine, 110-86-1; *o*-xylene, 95-47-6; *cis*- β -ocimene, 3338-55-4; styrene, 100-42-5; methyl hex-2-enoate, 2396-77-2; dimethylformamide, 68-12-2; octan-3-ol, 589-98-0; methyl octanoate, 111-11-5; methyl (methylthio)acetate, 16630-66-3; *cis*-linalool oxide (5-membered ring), 5989-33-3; *trans*-linalool oxide (5-membered ring), 34995-77-2; linalool, 78-70-6; benzaldehyde, 100-52-7; methyl furoate, 1334-76-5; methyl decanoate, 110-42-9; methyl benzoate, 93-58-3; phenylacetaldehyde, 122-78-1; *cis*-linalool oxide (6-membered ring), 14009-71-3; methyl nicotinate, 93-60-7; methyl dodecanoate, 111-82-0; hexanoic acid, 142-62-1; benzyl alcohol, 100-51-6; benzyl butanoate, 103-37-7; 2-phenylethanol, 60-12-8; phenylacetone nitrile, 140-29-4; δ -octalactone, 698-76-0; methyl tetradecanoate, 124-10-7; octanoic acid, 124-07-2; benzyl but-2-enoate, 65416-24-2; benzyl isothiocyanate, 622-78-6.

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