

## COMPARISON OF THE VOLATILE COMPONENTS OF SOME MANGO CULTIVARS

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**Key Word Index**—*Mangifera indica*; Anacardiaceae; mango; aroma volatiles.

**Abstract**—Three cultivars of mango from Sri Lanka (Jaffna, Willard and Parrot) were analysed for their volatile aroma components. The total concentrations of volatiles obtained were ca 251, 422 and 628  $\mu\text{g}$  per kg of fresh fruit, respectively. Terpenes were the main volatiles of all three cultivars, with monoterpene hydrocarbons contributing 50–63 % w/w of the total volatiles and sesquiterpene hydrocarbons 14–19 %. Whilst the major volatile of Jaffna mango was *cis*- $\beta$ -ocimene (38 %),  $\alpha$ -terpinolene was the major volatile of the other two cultivars (32 % and 35 %). Esters were produced by all cultivars (2–16 %), Jaffna yielding most, the majority being unsaturated (12 %). Willard mango gave particularly high levels of non-terpene hydrocarbons (19 %), including a range of six long-chain alkanes (8 %), not detected in the other cultivars.

### INTRODUCTION

Mango (*Mangifera indica* L.), one of the most popular and delicious of all tropical fruits, is probably also the most widely cultivated fruit for fresh market use [1]. Despite this importance, and the fact that in recent years the fruit and various processed products have become increasingly popular in Europe, there is relatively little information regarding the aroma and flavour constituents of mango. The work of Gholap and Bandyopadhyay [2–6] and of Hunter *et al.* [7] was summarized in our previous paper on mango volatiles [8], but more recent data have been reported by Diaz [9], Abd El-Baki *et al.* [10] and Pickenhagen *et al.* [11]. There are hundreds of mango cultivars (not all grown on a commercial scale) which exhibit a wide range of flavour. Each of the common cultivars reputedly has distinguishing flavour characteristics [1]. These factors may partly account for the major differences in aroma components which have been reported in the above-mentioned publications, and which otherwise would be unexpected for a single fruit. For example, car-3-ene was determined as the main volatile constituent from Venezuelan mango (an unnamed cultivar) [8], whilst this compound has not been detected in certain Indian cultivars, including the well-known Alphonso, in which *cis*-ocimene or myrcene is generally the major component [4, 5]. Conversely, myrcene could not be detected in the Venezuelan mango [8].

To evaluate further, and more systematically, the variation of aroma volatiles with cultivar, a more extensive survey of mango volatiles was undertaken, comparing three very different cultivars from Sri Lanka. These were selected to cover a number of variables. Two cultivars (Parrot or Giva Amba, and Willard) mature at the same time of year (May–July, the main mango season) and are considered to afford extremes of mango flavour. The third cultivar (Jaffna or Karutha Kolomban) has a different flavour, matures in October/November, and is a dry zone cultivar, particularly used for canning in Sri Lanka.

### RESULTS AND DISCUSSION

Fresh ripe mangoes were obtained from local markets in Colombo, Sri Lanka; the three cultivars are readily distinguishable by their external appearance. Valid aroma extracts were prepared the same day using well-established methods [8]. The extracts were concentrated [8], and then analysed by GC and by GC/EIMS and GC/CIMS. Duplicate analyses (Table 1) were carried out in all cases. 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 BP1 (equivalent to OV 101) or BP20 (equivalent to PEG 20M) stationary phase. The retention data given in Table 1 were obtained using a 25 m fused silica column coated with PEG 20M. Kováts retention indices [12, 13] 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 obtained 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. Reference spectra of most constituents are in general compilations of mass spectra [13, 14], but there are also very useful, more specific collections of spectra of monoterpene hydrocarbons [15] and sesquiterpene hydrocarbons [16]. The mass spectrum of germacrene D has been individually reported [17] and agreed very well with that obtained in this work.

The quantitative data in Table 1 show that in total ca 251, 422 and 628  $\mu\text{g}$  of aroma components were obtained per kg of fresh fruit (excluding skin and stone) for Jaffna, Willard and Parrot cultivars of mango, respectively. Our previous analysis of Venezuelan mango using similar methods [8] yielded only ca 60  $\mu\text{g}/\text{kg}$  of aroma components. These data do not necessarily mean that the Sri

Table 1. Volatile constituents of three cultivars of mango

Component	$R_i$ (min)	Kováts index (lit.)*	Jaffna			Mango cultivar			Parrot	Odour quality
			% Rel. abund.	$\mu\text{g/kg}$	% Rel. abund.	% Rel. abund.	$\mu\text{g/kg}$	% Rel. abund.		
Cyclohexane	0.7	765	—	—	—	—	—	tr	tr	—
Dimethyl sulphide	0.8	780	—	—	1.9	8.0	—	4.4	27.6	Sulphurous, cabbage-like
Methylcyclohexane	1.0	800	0.3	0.8	tr	tr	tr	0.2	1.3	—
Acetone	1.1	810	—	—	tr	tr	tr	tr	tr	—
Ethyl acetate	1.4	872	0.3	0.8	1.3	5.5	—	tr	tr	Fruity, ester
Pentan-2-one	1.6	969	0.1	0.3	—	—	—	—	—	—
Methyl butanoate	1.7	975	0.2	0.5	0.4	1.7	—	0.2	1.3	Estery, floral
Ethyl butanoate	1.9	1025	tr	tr	tr	tr	tr	tr	tr	Fruity, apples
$\alpha$ -Pinene	2.0	1039	0.7	1.8	6.6	27.9	1.6	1.6	10.0	Pine, cedar wood
Toluene	2.2	1055	2.7	6.8	9.8	41.4	3.6	3.6	22.6	Caramel, solvent
Hexanal	2.4	1084	0.4	1.0	—	—	—	—	—	Green grass, hexanal
An ethyl butenoate	2.7	—	2.3	5.8	—	—	—	—	—	Estery, acidic
Pent-3-en-2-one	2.8	1100	—	—	2.2	9.3	—	—	—	Toffee, burnt
$\beta$ -Pinene	3.0	1124	2.9	7.3	2.1	8.9	2.7	2.7	17.0	Polish, varnish
<i>m</i> -and/or <i>p</i> -Xylene	3.2	~1145	—	—	—	—	—	tr	tr	Stale, cold meat
Myrcene	3.3	1156	4.3	10.8	1.4	5.9	2.2	2.2	13.8	Fresh, green grass
Car-3-ene	3.4	1165	—	—	2.7	11.4	11.7	11.7	73.5	Green, pungent, mango leaves
Heptan-2-one	3.7	1172	0.2	0.5	—	—	—	—	—	—
Methyl hexanoate	3.8	1177	0.3	0.8	—	—	—	—	—	Ester, pear drops
$\alpha$ -Terpinene	3.9	1192	—	—	1.4	5.9	3.9	3.9	24.5	Floral, fragrant
Limonene	4.2	1206	2.6	6.5	3.8	16.0	3.1	3.1	19.5	Lemon-like
Butyl butanoate	4.3	1207	2.0	5.0	—	—	—	—	—	Green, fresh
Allo-ocimene	4.7	—	1.2	3.0	—	—	—	—	—	Floral, fragrant
<i>cis</i> - $\beta$ -Ocimene	4.9	1228	37.9	95.1	1.0	4.2	1.9	1.9	11.9	Fragrant, herbal
? A vinyl butenoate	5.1	—	1.2	3.0	—	—	—	—	—	Fruity, caramel
<i>trans</i> - $\beta$ -Ocimene	5.2	1250	—	—	—	—	—	0.8	5.0	—
<i>p</i> -Cymene	5.4	1272	tr	tr	tr	tr	tr	0.1	0.6	Estery, floral
$\alpha$ -Terpinolene	5.5	1287	tr	tr	32.1	135.5	35.0	35.0	219.8	Floral, fragrant
<i>cis</i> -Hex-3-en-1-yl acetate	5.9	1300	4.1	10.3	1.2	5.1	—	—	—	Fruity, pear
Hexan-1-ol	6.2	1316	0.6	1.5	0.5	2.1	—	—	—	Fruity, green
<i>cis</i> -Hex-3-en-1-ol	6.7	1351	3.4	8.5	1.3	5.5	0.7	0.7	4.4	Green grass, fruity, hexenol
<i>trans</i> -Hex-2-en-1-ol	6.9	1368	0.3	0.8	—	—	—	—	—	Green, sweet
<i>cis</i> -Hex-3-en-1-yl propanoate	7.0	1371	0.1	0.3	—	—	—	—	—	—
Hexyl butanoate	7.3	1398	0.6	1.5	—	—	—	—	—	Fruity, ester
Tetradecane	7.4	1400	—	—	tr	tr	tr	tr	tr	—

A dimethylstyrene	7.5	—	—	—	0.8	3.4	0.4	2.5	Mango
Ethyl octanoate	7.6	1423	0.3	0.8	—	—	—	—	Slightly nutty
cis-Hex-3-en-1-yl butanoate	7.8	1450	3.5	8.8	2.2	9.3	1.5	9.4	Fruity, ester
p-Cymen-8-ol	7.9	—	—	—	—	—	0.1	0.6	—
An acetylfuran	8.3	~1490	0.4	1.0	—	—	—	—	Floral, fragrant
Linalool	8.5	1506	—	—	—	—	tr	tr	Lemon peel
$\alpha$ -Copaene	8.7	1520	3.6	9.0	0.9	3.8	—	—	Earthy, mango
cis-Hex-3-en-1-yl pentanoate	8.9	1548	0.7	1.8	—	—	—	—	Fruity, caramel
$\alpha$ -Gurjunene	9.1	1558	1.7	4.3	0.6	2.5	0.8	5.0	Musty
Nona-2,6-dienal	9.4	—	2.6	6.5	—	—	—	—	Oily, fatty
$\beta$ -Elenene	9.6	1595	—	—	—	—	0.3	1.9	Floral, fragrant
Hexadecane	9.7	1600	—	—	0.2	0.8	—	—	—
$\beta$ -Caryophyllene	9.8	1618	4.6	11.5	2.4	10.1	1.0	6.3	Sickly sweet, fragrant, wallflowers
Phenylacetaldehyde	10.0	1646	1.4	3.5	—	—	—	—	Floral, fragrant, hyacinth
cis-Hex-3-en-1-yl hexanoate	10.1	1654	0.3	0.8	1.0	4.2	—	—	Sweet, ester
$\alpha$ -Terpineol	10.2	1661	tr	—	—	—	—	—	Slightly caramel, fragrant
Sesquiterpene hydrocarbon	10.4	—	0.4	1.0	—	—	—	—	—
$\alpha$ -Humulene	10.6	1682	2.6	6.5	1.4	5.9	1.2	7.5	Fresh green, floral
Hepiadeane	10.8	1700	—	—	1.7	7.2	—	—	Mouldy, fatty
Germacrene D	11.0	1718	0.8	2.0	—	—	—	—	Oily, nutty
$\alpha$ -Murolene	11.1	1725	—	—	0.6	2.5	1.5	9.4	Flat, earthy
$\beta$ -Selinene	11.2	1730	—	—	7.7	32.5	14.1	88.5	Nutty, dry grass, hay
4-Methylacetophenone	11.4	1750	—	—	—	—	0.7	4.4	Fruity
Naphthalene	11.5	—	0.3	0.8	—	—	—	—	Camphor
$\gamma$ -Cadinene	11.6	1766	0.6	1.5	—	—	tr	tr	Fragrant
Carboxylic acid	11.7	—	—	—	0.2	0.8	—	—	—
Benzothiazole	12.3	—	—	—	0.1	0.4	tr	tr	—
Octadecane	12.5	1800	—	—	2.0	8.4	—	—	Mouldy, dull, meaty
Ethyl dodecanoate	12.8	1826	tr	tr	tr	tr	—	—	Slight mango
$\gamma$ -Octalactone	13.2	1883	—	—	—	—	0.3	1.9	Sour
Carboxylic acid	13.8	—	—	—	—	—	tr	tr	—
Nonadecane	13.9	1900	—	—	1.9	8.0	—	—	Fragrant, dull
Sesquiterpene	14.0	—	tr	tr	—	—	—	—	—
Sesquiterpene alcohol	14.7	—	—	—	—	—	—	—	Lemon
Phenylacetoneitrile	15.1	—	0.4	1.0	—	—	1.2	7.5	—
Eicosane	15.2	2000	—	—	2.3	9.7	—	—	Flat, dull
Ethyl tetradecanoate	15.6	2027	tr	tr	0.1	0.4	—	—	—
$\delta$ -Decalactone	17.1	2144	—	—	—	—	0.1	0.6	—
Ethyl hexadecanoate	18.1	2222	tr	tr	—	—	—	—	—
Octanoic acid	18.8	—	2.5	6.3	—	—	—	—	—
Hexadecan-1-ol	19.5	—	3.8	9.5	3.9	16.5	4.3	27.0	—

\* Literature = [12, 13]; tr = trace (&lt; 0.1 %).

Lankan cultivars have a stronger aroma or flavour, since relative odour intensities of different constituents will, of course, affect the total perceived intensity, but in general terms all these concentrations are relatively modest.

Table 1 shows that 76 compounds were identified in Sri Lankan mangos (49 in Jaffna, 40 in Willard and 38 in Parrot), including 8 which were only partially characterized. The numbers of unidentified components and their total percentage contributions to the samples were 14 (0.8%), 6 (0.3%) and 12 (0.4%), respectively. The majority of these components were present in such small amounts that mass spectra could not be obtained, even using packed columns and high sample loadings. A number of significant differences can be observed between the results for the three cultivars, and to facilitate subsequent discussion, Table 2 summarizes quantitative data for some classes of compounds and for some important individual components. Data from the previous analysis of Venezuelan mango [8] are also included for comparison.

Table 2 shows that terpenes comprised the main volatiles of all cultivars studied. The numbers of such compounds and the total percentages were surprisingly similar for three cultivars, and Parrot mango showed only slightly higher levels. However, within this group of compounds there are important and appreciable dif-

ferences between the cultivars. Thus, Jaffna mango produced mainly *cis*- $\beta$ -ocimene, Venezuelan mango produced mainly car-3-ene, and the other two cultivars contained mainly  $\alpha$ -terpinolene (and in similar percentages). It is noticeable that those cultivars which did not yield  $\alpha$ -terpinolene as their major constituent contained only traces or none. Similarly, the cultivars which did not contain *cis*- $\beta$ -ocimene as their major constituent yielded only relatively small quantities. However, car-3-ene, the main volatile of Venezuelan mango, was also produced in relatively large amounts by Parrot mango, although it could not be detected at all in the Jaffna cultivar. Taking into account the strong and characteristic aromas of monoterpene hydrocarbons, these simple differences partly explain the known differences in flavour between these cultivars.

It is interesting that Jaffna mango, which is cultivated in the north of Sri Lanka nearest to India, was the only cultivar studied which contained either *cis*- $\beta$ -ocimene or myrcene as its major constituent, since these compounds are characteristic of some Indian cultivars [4, 5]. Myrcene was not a major component of any Sri Lankan cultivar and it could not be detected at all in Venezuelan mango [8]. It is possible that the common formation of high levels of  $\alpha$ -terpinolene in both Willard and Parrot cul-

Table 2. Quantitative data for some classes of aroma compounds and for specific important volatile constituents of three cultivars of mango from Sri Lanka and one from Venezuela

Compound	Jaffna		Mango cultivar		Parrot		Venezuelan [8]	
	% Rel. abund.	$\mu\text{g/kg}$	% Rel. abund.	$\mu\text{g/kg}$	% Rel. abund.	$\mu\text{g/kg}$	% Rel. abund.	$\mu\text{g/kg}$
Monoterpene hydrocarbons	49.6	124.6	51.1	215.6	63.0	395.5	55.0	33.6
Sesquiterpene hydrocarbons	14.3	35.9	13.6	57.4	18.9	118.7	13.9	8.5
Non-terpenoid hydrocarbons (total)	3.3	8.3	18.7	78.9	4.2	26.4	9.3	5.7
straight-chain alkanes	—	—	8.1	34.2	—	—	—	—
Alcohols	8.1	20.4	5.7	24.1	7.6	47.7	—	—
Aldehydes	4.4	11.1	—	—	—	—	16.9	10.3
Ketones	0.7	1.8	2.2	9.3	0.7	4.4	3.1	1.9
Esters (total)	15.9	40.0	6.2	26.2	1.7	10.7	—	—
unsaturated	12.2	30.7	4.4	18.6	1.5	9.4	—	—
Lactones	—	—	—	—	0.4	2.5	—	—
$\alpha$ -Pinene	0.7	1.8	6.6	27.9	1.6	10.0	8.2	5.0
$\beta$ -Pinene	2.9	7.3	2.1	8.9	2.7	17.0	—	—
Myrcene	4.3	10.8	1.4	5.9	2.2	13.8	—	—
Car-3-ene	—	—	2.7	11.4	11.7	73.5	26.0	15.9
Limonene	2.6	6.5	3.8	16.0	3.1	19.5	6.0	3.7
<i>cis</i> - $\beta$ -Ocimene	37.9	95.1	1.0	4.2	1.9	11.9	2.6	1.6
$\alpha$ -Terpinolene	tr	tr	32.1	135.5	35.0	219.8	—	—
$\gamma$ -Terpinene	—	—	—	—	—	—	7.7	4.7
$\beta$ -Selinene	—	—	7.7	32.5	14.1	88.5	8.7	5.3
Germacrene D	0.8	2.0	—	—	—	—	—	—
Dimethyl disulphide	—	—	1.9	8.0	4.4	27.6	tr	tr
Benzothiazole	—	—	0.1	0.4	tr	tr	—	—
Hexadecan-1-ol	3.8	9.5	3.9	16.5	4.3	27.0	—	—
A dimethylstyrene	—	—	0.8	3.4	0.4	2.5	6.2	3.8

tr = Trace (< 0.1%).

tivars could be partly associated with their seasonal similarity, but further study of other cultivars maturing at the same time would, of course, be necessary to substantiate this suggestion.

With regard to sesquiterpenes,  $\beta$ -selinene showed an interesting variation. It was produced in relatively large amount by Parrot mango, in about half this quantity by the Willard cultivar, but was not detectable at all from Jaffna mango. On the other hand, the Jaffna cultivar was the only one to yield the relatively uncommon sesquiterpene germacrene D.

The variation of other terpene constituents, for example,  $\alpha$ - and  $\beta$ -pinene, limonene and  $\gamma$ -terpinene, between the four samples can be seen in Table 2. It is of note that  $\gamma$ -terpinene was only detected in Venezuelan mango. Thus, overall, there are considerable differences in terpene volatiles between these mango cultivars.

Although non-terpenoid compounds were produced in lesser amounts than terpenes, there were, nevertheless, appreciable differences between the cultivars which would be expected further to affect flavour. This is particularly seen with the esters. Jaffna mango contained 17 esters which together accounted for 15.9% of the sample, whilst the Willard cultivar contained only eight, contributing 6.2%, and the Parrot cultivar only four, contributing 1.7%. No esters could be detected in Venezuelan mango [8]. The most abundant esters were unsaturated (12.2% of the sample for Jaffna mango), and included a range of derivatives of *cis*-hex-3-en-1-ol (from acetate to hexanoate, inclusive). Such compounds are well known as aroma volatiles. There was also a large variation between cultivars in the content of non-terpene hydrocarbons. Willard mango yielded far more than any other cultivar, and in particular it gave a range of six straight-chain alkanes from tetradecane to eicosane, none of which was detected in any other cultivar.

Other, possibly important, differences between the cultivars include the following. Willard was the only cultivar to give pent-3-en-2-one, and in quite large amount. Lactones, which have been reported previously in canned mango [7], were only produced by Parrot mango, but in small quantities. Of the Sri Lankan cultivars, only Jaffna produced any aldehydes (three). The high percentage given by Venezuelan mango was mainly due to furfural, which was not detected in the present work. The two sulphur compounds could not be detected in the Jaffna cultivar, and only traces of dimethyl sulphide were obtained from Venezuelan mango and no benzothiazole. The other two cultivars produced both sulphur compounds, with Parrot mango yielding appreciable quantities of dimethyl sulphide. All Sri Lankan cultivars gave relatively large amounts of one long-chain alkan-1-ol. This was not produced by Venezuelan mango, in which no alcohols were detected.

The dimethylstyrene, which was identified in Venezuelan mango in relatively large concentration [8], was also detected in the Willard and Parrot cultivars, but not in Jaffna mango. From the mass spectrum of this compound, it is not possible to assign fully the positions of the methyl substituents, but they are nuclear. From odour descriptions at an odour port during GC analysis, the dimethylstyrene was described as having mango character, both in this work and in the previous study [8]. In agreement with the earlier investigation [8], car-3-enc was again described as having significant mango quality, but in addition in this work the GC peaks due to  $\alpha$ -copaene and

ethyl dodecanoate were also considered to have mango character.

## EXPERIMENTAL

**Sample preparation.** Fresh ripe mangoes were obtained from local markets in Colombo, Sri Lanka and were extracted the same day using a modified [18] Likens and Nickerson apparatus [19], as previously described for Venezuelan mango [8]. Pentane (15 ml) was used as solvent and extraction was carried out for 2 hr. Extracts were subsequently concd to 1.0 ml as previously described [18].

**GC. FID-GC:** 25 m  $\times$  0.2 mm i.d. fused silica capillary containing PEG 20M or OV 101 or BP20 bonded-phase (equivalent to PEG 20M) or BP1 bonded-phase (equivalent to OV 101);  $H_2$  0.8 ml/min; temp. programme 65° for 3 min, followed by an increase at 12°/min to 180°; detector and injection point heaters, 275° and 250°, respectively; typically 0.1  $\mu$ l or 1.0  $\mu$ l injected at 25:1 split. Other 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, using  $N_2$  (30 ml/min) and the same temp. programme.

**GC/MS.** A Kratos MS25 instrument was used, linked on-line to a Kratos DS50 data processing system. The same GC conditions as above were used, with He as carrier gas. Packed columns and bonded-phase fused silica columns were mainly used. The single-stage all-glass jet separator was at 250°. Significant operating parameters of the MS during EIMS were: ionization voltage, 70 eV; ionization current, 100  $\mu$ A; source temp., 225°; accelerating voltage, 1.33 kV; resolution, 1500; scan speed, 1 sec/decade (repetitive throughout run). Identical conditions were employed during CIMS except for: reagent gas, *i*-butane; 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 analysed. Quantitative data were then derived both from the TIC trace during GC/MS and from the GC-FID traces. Known amounts of a selection of identified compounds (toluene, limonene, *cis*-hex-3-en-1-ol and hexadecan-1-ol) were injected under the same analytical conditions in order to enable calculation of absolute amounts of components in the sample.

**Odour assessment.** Aromas of the separated components of the essences were assessed at an odour port following GC. An outlet splitter at 10:1 diverted the major fraction of the eluate through a heated line to the outside of the GC oven for aroma assessment by two subjects, both of whom were familiar with mango aroma.

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