VOLATILE AROMA CONSTITUENTS OF MANGO (cv KENSINGTON)

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Abstract—The aroma volatiles of the Kensington cultivar of mango were analysed using routine procedures, and results compared with those for other cultivars. In total, 58 constituents were positively identified, including 36 not previously reported for this cultivar, and seven not previously described for any cultivar of mango. Monoterpene hydrocarbons were the major group of volatiles (at *ca* 49% w/w of the total volatiles) with α-terpinolene as the most abundant single constituent (*ca* 26%), but esters were unusually also major components (16, *ca* 33%). The latter probably contribute to the unique mango flavour of this cultivar, together with certain lactones important in peach flavour.

INTRODUCTION

In the last few years there has been a number of detailed studies of the aroma volatiles of mango fruit (*Mangifera indica* L.) [1–7], following the earlier work of Gholap and Bandyopadhyay in India [8–12]. However, there are literally hundreds of different cultivars of mango, grown in various parts of the world, which exhibit a wide range of flavour. Each of the common cultivars reputedly has distinguishing flavour characteristics [13], and the previous work has shown considerable variation in the nature of the aroma volatiles between different cultivars [1–12]. There is thus still much scope for further investigation of mango aroma volatiles.

One cultivar of especial interest is called Kensington or Kensington Pride. This particular cultivar is somewhat unusual in being indigenous to Australia (mango originated in the Indo-Burmese region), where it is known as 'Bowen' mango. Its flavour is supposed to be unique in comparison with other mangoes, and the fruit is highly prized in Australia. Recently, we have studied some cultivars of mango grown in Florida [5], and since the Kensington mango is also cultivated there, it was decided to examine its aroma volatiles and to compare them with results for other cultivars. A report has very recently appeared listing some of the aroma volatiles of this cultivar grown in Queensland, Australia [14].

RESULTS AND DISCUSSION

The Kensington cultivar of mango used in this work was introduced to Florida from St Croix in the Virgin Islands in 1962; in turn, that stock had originated in Queensland, Australia. Fresh, ripe mangoes were shipped by air freight to London from Miami, and valid aroma extracts were prepared immediately using well established procedures [1, 3, 5, 15]. The odour quality of the extracts was genuine Kensington mango, with sweet, fruity and estery notes. The fresh fruit itself was similarly

described, with noticeable peach and lactone-type character. The extracts were concentrated by high vacuum-low temperature distillation [1, 3, 5, 15], and the resultant essence was found, on appropriate re-dilution, to possess the strong characteristic Kensington mango aroma.

The sample was analysed by GC and GC/MS, and results are given in Table 1. Fused silica capillary GC columns were used, containing either bonded-phase BP1 (equivalent to OV 101) or BP20 (equivalent to PEG 20M). The retention data given in Table 1 were obtained using a 25 m fused silica column (BP20). Literature Kováts retention indices [16, 17] of most components (on PEG 20M) are also included in the Table, and confirm the general elution sequence. The qualitative data in Table 1 were obtained using both capillary columns; some components were more readily identified by GC/MS using one particular phase. Where positive identities are given, the mass spectra obtained on GC/MS agreed with those in the literature.

The quantitative data in Table 1 show that in total about 13 μg of aroma components were obtained per gram of fresh fruit (excluding stone). This is an intermediate concentration compared with our previous analyses, where levels of less than 1 μg/g have often been found [1, 3], but amounts as high as 54 and 72 μg/g were determined for other cultivars of mango grown in Florida [5]. Engel and Tressl obtained 41 and 90 μg/g total volatiles for Alphonso and Baladi mango, respectively [2], and Idstein and Schreier reported 57 μg/g for Alphonso [4]. Bartley and Schwede do not give any absolute quantitative data with regard to their analysis of Kensington mango [14].

Overall, we detected 91 components as Kensington mango volatiles, of which 58 (comprising *ca* 96.2% w/w of the sample) were positively identified, with a further 18 (*ca* 2.7%) partially characterized. The 15 (*ca* 1.1%) unidentified components are not included in Table 1, and were present in the sample in such low amounts that

Table 1. Volatile components of Kensington mango

Component	New	R_t (min)	Kováts index (lit.)*	Rel. abund.† (%)	Amount (µg/g fresh tissue)
Dimethyl sulphide	+	1.2		2.1	0.27
Acetaldehyde	‡		(690)	tr	tr
Cyclohexane	+	‡	(765)	tr	tr
Ethyl acetate		1.6	872	5.5	0.72
1,1-Diethoxyethane	+	‡	(880)	0.1	0.01
Ethanol	+	1.7	900	0.4	0.05
Ethyl propanoate	+	1.8	944	0.3	0.04
Methyl butanoate	+	2.1	975	0.2	0.03
Butyl formate	+	2.2	996	tr	tr
α-Thujene		2.3	1025	2.6	0.34
Ethyl butanoate		2.6	1025	16.8	2.18
Pentane-2,3-dione	+	2.7	1044	0.1	0.01
Butyl acetate		2.8	1059	0.2	0.03
Hexanal	+	2.9	1084	0.6	0.08
Unsaturated C_6 ester		3.6		0.8	0.10
2-Methylbutan-1-ol	+	‡		tr	tr
Car-2-ene	+	3.9		1.0	0.13
Camphene	+	4.0	1083	0.9	0.12
Butan-1-ol		4.1	1113	tr	tr
Sabinene	+	4.2	1130	1.1	0.14
Car-3-ene		4.3	1140	7.4	0.96
Myrcene		4.6	1156	1.6	0.21
Ethyl but-2-enoate		4.8	1161	4.7	0.61
α-Terpinene		5.1	1188	3.2	0.42
Limonene		5.4	1206	2.1	0.27
β-Phellandrene		5.5	1216	1.6	0.21
trans-Hex-2-enal	+	6.2	1207	1.2	0.16
Ethyl hexanoate plus cis-β-ocimene	+	6.6	1223 1228	0.4	0.05
γ-Terpinene	+	7.3	1251	0.6	0.08
Terpene		7.4		0.1	0.01
p-Cymene		7.9	1272	0.2	0.03
α-Terpinolene		9.3	1287	26.3	3.42
Terpene		10.0		tr	tr
Terpene		10.2		tr	tr
Hexan-1-ol		11.0	1316	0.7	0.09
cis-Hex-3-en-1-ol	+	12.1	1351	1.3	0.17
C_4-alkylbenzene		12.5		0.4	0.05
C_4-alkylbenzene		13.7		0.4	0.05
4-Isopropenyl-1-methylbenzene		14.0		0.8	0.10
Ethyl octanoate		14.2	1423	0.9	0.12
Unsaturated C_4-alkylbenzene		‡		0.3	0.04
Furfural	+	15.2	1449	0.3	0.04
Unsaturated C_4-alkylbenzene		‡		tr	tr
Sesquiterpene hydrocarbon		16.3		0.1	0.01
2-Acetylfuran	+	16.8	1491	tr	tr
α-Copaene	+	17.9	1520	0.5	0.07
Terpene		18.8		0.1	0.01
Terpene		19.3		tr	tr
5-Methylfurfural	+	19.9	1563	tr	tr
Sesquiterpene hydrocarbon		‡		0.4	0.05
β-Caryophyllene		20.3	1618	1.3	0.17
Terpene		22.4		tr	tr
Ethyl decanoate		22.5	1624	0.3	0.04
α-Humulene		23.0	1682	1.2	0.16
Geranial	+	24.3	1730	0.3	0.04
Terpene		24.6		tr	tr
Terpene		25.6		tr	tr
4-Methylacetophenone		27.3	1750	tr	tr

Table 1. Continued

Component	New	R_t (min)	Kováts index (lit.)*	Rel. abund.† (%)	Amount (µg/g fresh tissue)
Carveol	+	29.3	1805	0.3	0.04
Ethyl dodecanoate	+	30.1	1826	tr	tr
p-Cymen-8-ol	+	30.2		1.4	0.18
5-Butyldihydro-3H-furan-2-one	+	32.3	1883	1.3	0.17
2,6-Di-t-butyl-4-ethylphenol	+	32.5		0.1	0.01
Methylketone		36.0		tr	tr
Pentadecanal	+	36.5	~2010	tr	tr
Ethyl ester		36.8		tr	tr
Ethyl tetradecanoate	+	37.3	2027	1.2	0.16
Hexadecanal	+	39.7	~2115	0.5	0.07
Dihydro-5-hexyl-3H-furan-2-one	+	40.0	2101	0.3	0.04
6-Pentyltetrahydro-2H-pyran-2-one	+	41.6	2144	0.1	0.01
Ethyl hexadecanoate	+	44.2	~2225	0.6	0.08
Sesquiterpene alcohol		48.1		0.1	0.01
Dihydro-5-octyl-3H-furan-2-one	+	48.7	2317	0.2	0.03
Hexadecyl acetate		49.7	~2300	1.3	0.17
Octadecanal	+	50.1	~2330	0.1	0.01

* Lit. [15, 16].
†Quantitative data are derived from duplicate analyses and agreed ± 1%.
‡ Detected in BP1 run only.
tr, Trace.

either no mass spectrum could be recorded or the spectrum was too poor for interpretation. Of the fully identified components, 36 are reported as Kensington mango volatiles for the first time, and these are indicated in Table 1 by '+'. However, as already indicated, there has been only one previous study of this cultivar of mango [14]. Nevertheless, eight of the constituents listed in Table 1 are also newly reported volatiles for any cultivar of mango, namely, butyl formate, pentane-2,3-dione, 2-methylbutan-1-ol, car-2-ene, 2,6-di-t-butyl-4-ethylphenol, hexadecyl acetate, pentadecanal and octadecanal. The latter three components are high boiling, late eluting compounds, which could have been easy to miss in earlier analyses. Of the others, three are worthy of brief comment.

With regard to the formate, Idstein and Schreier have already detected two formates in mango, namely, the 3-methylbutyl and the hex-3-enyl [4], and commented on the fact that formates are rarely found in nature [18, 19]. It is interesting, therefore, that yet another has now been detected in mango. Car-2-ene is relatively uncommon terpene and infrequently reported as an aroma volatile [20]. The identification here was confirmed by comparison with a reference sample. Although listed in Table 1, 2,6-di-t-butyl-4-ethylphenol is unlikely to be a genuine aroma volatile of mango. It is the higher homologue of the methylphenol, the well-known antioxidant BHT. Not surprisingly, 2,6-di-t-butyl-4-ethylphenol also has antioxidant properties, and it is permitted by the FDA in the U.S.A. under the U.S. Food Drug and Cosmetic Act for use as an antioxidant and/or stabilizer in ethylene polymers and co-polymers intended for contact with foods [21]. Since the Kensington mangoes were transported from the U.S.A. individually wrapped in polythene bags, the likely origin of this contaminant is obvious, but it is

perhaps surprising that migration of the antioxidant was so rapid.

It can be seen from Table 1 that the most abundant group of aroma volatiles from this cultivar of mango was the monoterpene hydrocarbons (at ca 49% w/w of the total volatiles). This is in agreement with previous detailed studies of mango, although generally even higher levels have been found, ranging from ca 50 to ca 93% [1–5]. The reason for this lower concentration is that the Kensington cultivar is unusual in containing a relatively high amount of esters (ca 33%), although levels of ca 13% [2] and of ca 16% [3] have been reported previously for the Baladi and Jaffna cultivars, respectively. However, generally concentrations of esters in mango are much lower, but in the one previous study of the Kensington cultivar, Bartley and Schwede obtained no less than ca 68% [14]. They used a headspace analytical technique, and attributed the previously reported low levels of esters in mango to hydrolysis of esters during Likens and Nickerson extraction [14]. Clearly, from a chemical point of view, this is highly unlikely, and in previous use of the apparatus, very high concentrations of esters have frequently been recovered from other tropical fruits, e.g. 53% from papaya [22], 55% from guava [23] and 80% from soursop [24]. Furthermore, in a simple assessment of the apparatus by a model system, greater than 90% of ethyl acetate was recovered after 3 hr extraction, which was generally better than for certain other classes of compound [25].

However, there is no doubt that the Kensington cultivar of mango is unusual in possessing a high level of esters, and this will certainly contribute to its unique mango flavour. It is notable that in our flavour assessment of the fruit, we found it to have distinct ester character. Table 1 shows that ethyl butanoate was the

most abundant ester, and this agrees with the results of Bartley and Schwede, although they found a very high concentration (ca 45%) [14]. A reasonable amount of the unsaturated ethyl but-2-enoate was also detected (ca 5%), and it was the fifth most abundant component. Again, this constituent has already been reported for Kensington mango, but less than 1% was obtained [14]. It has always been recognised that esters, as well as monoterpene hydrocarbons, are important to mango flavour, and, for example, Engel and Tressl identified 25 and 24 (both saturated and unsaturated) in Alphonso and Baladi, respectively [2], and Idstein and Schreier detected 32 in Alphonso [4]. Even though in higher total concentration, we found only 16 in Kensington mango, an identical number to that previously reported [14].

Despite the great importance of the esters, as stated earlier about half of the total volatiles from Kensington mango, on a w/w basis, were monoterpene hydrocarbons, and indeed the most abundant constituent of all was α-terpinolene (at ca 26%). Bartley and Schwede also reported a high concentration of terpinolene (presumably the α-isomer) from Kensington mango, and a remarkably similar amount (ca 27%) [14]. This compound has already been found to be a major volatile of some cultivars of mango (at levels of ca 32 and 35%) [3]. Another important monoterpene hydrocarbon of some mango cultivars is car-3-ene, and this was the third most abundant constituent of Kensington mango at ca 7%. However, this compound has been determined at extraordinarily high levels in some Florida mangoes (ca 60 and 76%) [5], and the variation in the nature of the major monoterpene component between different mango cultivars has previously been discussed [3].

In comparison with the monoterpene hydrocarbons, generally fewer sesquiterpene hydrocarbons, and in lower concentration, have been found in mango [1–5], although totals as high as ca 19% have been reported [3]. However, Sakho et al. found no less than 16 sesquiterpene hydrocarbons totalling ca 31% of the total volatiles in the only study to date of African mangoes [6]. Eremophilene (not reported before or since in any other mango) was the most abundant sesquiterpene hydrocarbon at ca 18% of the total volatiles [6]. We could not detect this compound in our sample, but the amounts of sesquiterpene hydrocarbons were quite low (ca 3% in total), and only very common representatives were found.

A few lactones are listed in Table 1, namely, 5-butyl-, 5-hexyl- and 5-octyl- dihydro-3H-furan-2-ones (γ-octalactone, γ-decalactone and γ-dodecalactone, respectively), and 6-pentyltetrahydro-2H-pyran-2-one (δ-decalactone). None of these is new for mango, although all are new for the Kensington cultivar, and indeed many additional representatives have been previously reported [2, 4, 6]. In particular, Idstein and Schreier detected a large number of γ- and δ-lactones in Alphonso mango (14), and commented on the wide range and complexity of these in comparison with other fruits in which lactones are key constituents [4]. One fruit in which lactones do play an important rôle in flavour is peach [26], and it is relevant, therefore, that we detected a reasonable total concentration of lactones in Kensington mango when the fruit itself was described as having significant peach character. All four of the lactones which we detected in Kensington mango are major volatiles of peach [27, 28], and it is generally accepted that three of these in particular (γ-decalactone, δ-decalactone and γ-dodecalactone) are the most important contributors to peach flavour [29]. Bartley and Schwede could not detect any lactones in their analysis of Kensington mango, even by the use of single ion monitoring techniques, and so they suggest that such compounds are artefacts of the extraction procedures used by previous workers [14]. However, it is also possible that in using a low-sensitivity headspace analysis, any lactones present would be below detection limits.

In conclusion, the results presented in Table 1, in comparison with similar detailed studies of other mango cultivars, show a number of significant differences, sufficient to account for the unique mango flavour of the Kensington cultivar.

EXPERIMENTAL

Authentic Kensington mangoes were obtained from the Subtropical Horticultural Research Station in Miami, Florida, and were shipped by air freight to London for analysis.

Sample preparation. Ripe fruit (800 g) were extracted broadly as previously described for mango [1, 3, 5], using a modified [15] Likens and Nickerson apparatus [30]. Double distilled 2-methylbutane (30 ml) was used as solvent, and extraction was carried out for 3 hr. Two extractions were performed and the extracts combined before low temp.–high vacuum concentration to 100 μl, as previously described [15].

GC. FID-GC: 25 m × 0.2 mm i.d. fused silica capillary column coated with BP20 (or BP1) bonded phase; H_2, 1.2 ml/min; temp. prog., 70° for 5 min then 3°/min to 180°; detector and injection point heaters, 275° and 250°, respectively; injection vol., typically 0.1 μl at 25:1 split.

GC/MS. Capillary GC conditions as above were used, with He as carrier gas. The single-stage all-glass jet separator was at 250°. Significant operating parameters of the MS were: ionization voltage, 70 eV; ionization current, 100 μA; source temp., 225°; accelerating voltage, 1.33 kV; resolution, 1500; scan speed, 1 sec/decade (repetitive throughout run).

Quantitative assessment. Samples were prepared in such a manner that a known aliquot of the mango sample was analysed. Quantitative data were then derived both from the TIC monitor during GC/MS, and from the GC-FID trace during routine GC. EtOAc (0.050 M) was used as quantitative GC standard and corrections were made for the carbon-number of the identified constituents. An average correction factor was applied to unidentified GC peaks.

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