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Comparison of Free and Glycosidically Linked Volatile Components from Polyembryonic and Monoembryonic Mango (*Mangifera indica* L.) Cultivars

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Free and glycosidically linked volatile components of four mango cultivars of polyembryonic (M'Bingué and Tête de Chat) and monoembryonic (Amélie and Palmer) seed origins were examined. Eighty-five free volatile components were identified in the four cultivars, of which 33 are newly described as mango volatile compounds. Terpene hydrocarbons (104, 139, 26, and 35 mg/kg of fresh pulp, respectively) were the major volatiles of all four cultivars (>90% of the total volatiles), the dominant terpenes being (*Z,E*)-ocimenes (70%) in Amélie and car-3-ene (80%) in the other cultivars. Free oxygenated volatiles, mainly represented by monoterpenoids, and C_{13} norisoprenoids were present in all cultivars, the African Tête de Chat cultivar being by far the richest (12.3 mg/kg). Of the 29 aglycons characterized, 12 were identified for the first time as mango bound volatiles. Again, the Tête de Chat cultivar was the richest (2.1 mg/kg) with monoterpenoids and C_{13} norisoprenoids as the main glycosidically linked volatile compounds.

Keywords: *Mango; Mangifera indica L.; volatile; polyembryonic cultivars; monoembryonic cultivars*

INTRODUCTION

Mango (*Mangifera indica* L.; Anacardiaceae family) is grown throughout the tropics, where it is highly prized due to its attractive flavor, delicious taste, and nutritional value. In terms of world production mango is second only after bananas among tropical fruit (Anonymous, 1995). Hundreds of cultivars (cv.) are grown in various parts of the world, although few of them have any significant commercial impact. Mangoes originate either from trees of monoembryonic seed origin (e.g. most Indian cultivars) or from trees of polyembryonic seed origin (Purseglove, 1974). Both types are propagated vegetatively by grafting. Monoembryonic cultivars are grafted to maintain the cultivar characters and uniform commercial orchards since the seeds do not breed true to type. Polyembryonic cultivars, although they grow from seeds true to type, are grafted to produce early-bearing trees. Most fresh mangoes and mango-derived products sold on the world market originate from monoembryonic cultivars. Polyembryonic cultivars exist as either indigenous rain forest trees (Adedeji et al., 1992) or are grown in some parts of the world (Purseglove, 1974) for local consumption. In comparison with commercially important cultivars, polyembryonic mangoes exhibit a stronger turpentine-like aroma and a stringy flesh characterized by many distinct tough fibers (Purseglove, 1974). Although consumers from temperate countries find such flavor and texture characteristics disagreeable these polyembryonic cultivars deserve more attention as they might nonetheless serve as complementary raw material in the processing of commercial cultivars to enhance or modify the flavor of the finished product.

Several papers have been published on the volatile components of monoembryonic mango cultivars (Gholap and Bandyopadhyay, 1975; Diaz, 1980; Engel and Tressl, 1983a; Ackerman and Torline, 1984; MacLeod and Pieris, 1984; MacLeod and Snyder, 1985, 1988; Idstein and Schreier, 1985; Bartley and Schwede, 1987; MacLeod et al., 1988). Monoterpene and sesquiterpene hydrocarbons are the major volatile components of all mango cultivars (Winterhalter, 1991), representing 70–90% of total volatiles. However, their relative abundance is variable, (*Z*)-ocimene or β-myrcene being dominant in Indian cultivars, while car-3-ene is the major monoterpene in cultivars from the New World (MacLeod and Snyder, 1985). Alcohols, carbonyls, esters, lactones, acids, monoterpenoids, and C_{13} norisoprenoids are also present in mango but in far lower amounts than terpenes (TNO, 1996).

Glycosidically bound volatile components are also present in mango, but they have been characterized in only unknown polyembryonic cultivars (Adedeji et al., 1992; Koulibaly et al., 1992; Sakho et al., 1997). These authors named these mangoes of polyembryonic origin the African mango, which must not be confused with

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Irvingia gabonensis Baill (Irvingiaceae family), also called the African mango (Aina, 1990).

The aims of our study were to estimate the potential value of African polyembryonic cultivars in processing and to compare free and glycosidically bound volatile components from two polyembryonic mango cultivars with those of two monoembryonic commercial ones.

MATERIALS AND METHODS

Solvents and Chemicals. The solvents (*n*-pentane, dichloromethane, and ethyl acetate) were of analytical grade and were redistilled before use. Amberlite XAD-2 (20−60 mesh) was purchased from Fluka (Buchs, Switzerland) and washed with solvents before use according to the procedure of Gunata et al. (1985). Camphene (94% purity), 2-carene (97%), 1,5-dimethyl-1,5-cyclooctadiene (75%), longifolene (98+%), guaiazulene (99%), and a standard of *n*-paraffins (C_5-C_{35}) were from Aldrich Chimie S.a.r.l. (Saint Quentin Fallavier, France).

Fruits. Mango fruits from polyembryonic African cultivars (M'Bingué, and Tête de Chat) and monoembryonic commercial cultivars [Amélie (also known as Governor) and Palmer] were collected at the preclimacteric green mature stage (Medlicott et al., 1992) from trees in the CIRAD-IDEFOR experimental orchard of Korhogo (Ivory Coast), immediately air-freighted to France, and then delivered to our laboratory. Upon arrival, homogeneous batches (~200 kg for each cultivar) were brought to full ripeness, then pureed with simultaneous elimination of stones and skins, and refined (1 mm screen) (Ollé et al., 1996). Purees were stored in polyethylene bags at −20 °C until use.

Extraction of Terpene Hydrocarbons with Pentane. Puree aliquots (25 g) were thawed in 100 mL of cold pentane to which was added 100 μL of octan-2-ol as internal standard (2.98 mg/mL ethanol), and after thorough homogenization in a Potter Elvejhem homogenizer, phase separation was achieved by centrifugation at 9000*g* for 20 min (4 °C). The upper organic phase was recovered, dried over anhydrous sodium sulfate, and carefully concentrated to 4 mL using a Vigreux column (40 °C). Nonan-4-ol (100 μL at 3.04 mg/mL ethanol) was then added as the external standard prior to GC and GC/MS analyses. Each cultivar was analyzed in triplicate.

Extraction of Free and Bound Oxygenated Volatile Components. Puree aliquots (50 g) were thawed in 100 mL of cold 0.1 M phosphate buffer (pH 7, 4 °C) and thoroughly homogenized in a Potter Elvejhem homogenizer and 10 μL of octan-2-ol added as internal standard (2.98 mg/mL). After centrifugation at 9000*g* for 20 min (4 °C), the supernatant was percolated in the cold at 90 mL/h through a 35 × 1 cm i.d. column packed with 10 mL of Amberlite XAD-2 (Gunata et al., 1985). The column was then rinsed with 200 mL of Milli-Q water to eliminate water-soluble compounds. Free volatile compounds were recovered first by elution with 50 mL of azeotropic pentane/dichloromethane mixture (2:1, v/v), and then glycosidically bound volatile components were obtained by subsequent elution with 50 mL of ethyl acetate (Voirin et al., 1992). The fraction containing free volatile components was dried over anhydrous sodium sulfate and then concentrated to 0.4 mL using successively Vigreux and micro-Dufton columns (35 °C). The fraction containing bound volatile compounds was initially dried over anhydrous sodium sulfate and then under a nitrogen stream at 50 °C. The dried material was then dissolved in 0.1 mL of 0.1 M phosphate−citrate buffer (pH 5), and the buffered mixture was washed with 5 × 0.1 mL of azeotropic pentane/dichloromethane mixture. Then 0.1 mL was added of a mixture of 20 mg/mL of Pektolase 3PA (*Aspergillus niger*, Grinsted Products, Brabrand, Denmark) and 10 mg/mL of hemicellulase REG 2 (*A. niger*, Gist Brocades S.A., Seclin, France), in a phosphate−citrate buffer. Enzymatic hydrolysis of glycosides was performed for 16 h at 40 °C, and the released aglycons were extracted five times with azeotropic pentane/dichloromethane mixture (0.1 mL). After addition of 10 μL of octan-2-ol (2.98 mg/mL), the extract was concentrated to 0.4 mL as described above. Each cultivar was analyzed in triplicate.

GC Analysis. A Varian 3300 gas chromatograph was used with a flame ionization detector (FID), an on-column injector, and a DB-Wax (J&W Scientific, Folsom, CA) fused silica capillary column (30 m length, 0.32 mm internal diameter, 0.5 mm film thickness). Oven temperature was held at 40 °C for 3 min and then increased at a rate of 3 °C/min up to 245 °C, at which it was held for 20 min. Injector temperature was raised from 20 to 245 °C at 180 °C/min, at which it was held for 90 min. Detector temperature was 245 °C. Hydrogen was the carrier gas at 0.95 mL/min. Injected volumes were 1 μL of concentrated extract. Response factors were taken as 1.0 for all compounds with reference to octan-2-ol as internal standard. Linear retention indices were calculated with reference to *n*-paraffin standards (C_5-C_{35}).

GC/MS Analysis. A Hewlett-Packard 5890 gas chromatograph coupled to a Hewlett-Packard 5989A quadrupole mass spectrometer with an electron impact mode (EI) generated at 70 eV was used. The ion source temperature was 250 °C, and the filament emission current was 1 mA. The same column as above was used for separation. Oven temperature was held at 60 °C for 3 min and then increased at a rate of 180 °C/min up to 245 °C, at which it was held for 20 min. Injector was heated from 20 to 245 °C at 180 °C/min. Helium was the carrier gas at 1.1 mL/min. Electron impact mass spectra were recorded in the 29−350 amu range at 1 s/interval. Injected volumes were 1 μL of concentrated extract.

The molecular weight of some unknowns was obtained by chemical ionization (CI) using methane as the reagent gas. Compounds were identified on the basis of linear retention indices and EI or PCI mass spectra from the literature or from authentic standard compounds (Jennings and Shibamoto, 1980; Tressl et al., 1983; Adams, 1989; Schwab et al., 1989; Le Quere and Latrasse, 1990; Humpf and Schreier, 1991; Pabst et al., 1991; Hirata et al., 1994). Triplicate analyses were carried out in all cases.

RESULTS AND DISCUSSION

Since mango contains apolar terpene hydrocarbons and more polar oxygenated volatile compounds (Winterhalter, 1991; TNO, 1996) and because they cannot be properly obtained using only one technique, they were extracted separately using two complementary procedures. Terpene hydrocarbons were selectively extracted directly from the pulp by cold *n*-pentane to minimize rearrangements of these heat sensitive compounds (Sakho et al., 1985; Tesseire, 1986). Free and glycosidically bound oxygenated compounds were extracted simultaneously by adsorption chromatography on the nonionic Amberlite XAD-2 resin (Gunata et al., 1985) and separated by successive elutions with azeotropic pentane/dichloromethane mixture and ethyl acetate (Voirin et al., 1992).

Three exogenous monoterpenes and two sesquiterpenes absent from the studied cultivars were added to the pulp of cv. M'Bingué, and the terpenes were extracted accordingly. The extraction concentration yields measured using nonan-4-ol as the external standard were as follows: camphene (69%), 2-carene (72%), 1,5-dimethyl-1,5-cyclooctadiene (89%), longifolene (83%), guaiazulene (91%), and octan-2-ol (78%). Thus, octan-2-ol, having an intermediate behavior between the mono- and sesquiterpenes, was chosen as an appropriate internal standard and the results are expressed as octan-2-ol equivalents without consideration of extraction and concentration yields and FID response factors; that is, the calibration factor = 1.0 for all terpenes (Idstein and Schreier, 1985; Pino et al., 1989). The extraction−concentration yields of free and bound oxy-

Table 1. Distribution of Terpene Hydrocarbons in Cultivars M'Bingué, Tête de Chat, Amélie, and Palmer

		M'Bingué		Tête de Chat		Amélie		Palmer		
compound	LRI[a]	mg/kg	rel abundance (%)	mg/kg	rel abundance (%)	mg/kg	rel abundance (%)	mg/kg	rel abundance (%)	reliability of ID[e]
α-pinene + α-thujene	1021	1.5 (11)[b]	1.4	1.9 (9)	1.4	–[d]	–	0.4 (1)	1.1	1
β-pinene	1108	0.2 (31)	0.2	0.1 (6)	tr[c]	–	–	–	–	1
sabinene	1115	0.2 (19)	0.2	0.2 (9)	0.1	–	–	–	–	1
car-3-ene	1134	81.2 (6)	78.1	105.0 (1)	75.7	0.5 (9)	1.9	28.3 (9)	80.2	1
α-phellandrene + *β*-myrcene	1148	4.2 (3)	4.0	4.0 (2)	2.9	0.2 (17)	0.8	1.1 (9)	3.1	1
α-terpinene	1160	0.5 (6)	0.5	0.4 (14)	0.3	–	–	0.2 (17)	0.6	1
limonene	1184	2.4 (7)	2.3	2.6 (4)	1.9	–	–	0.7 (15)	2.0	1
β-phellandrene	1191	1.7 (12)	1.6	1.0 (8)	0.7	–	–	0.3 (10)	0.8	2
(*Z*)-ocimene	1224	–	–	–	–	18.6 (5)	71.3	–	–	1
γ-terpinene	1228	0.1 (16)	0.1	0.1 (30)	tr	–	–	–	–	1
(*E*)-ocimene	1235	0.1 (32)	0.1	0.2 (26)	0.1	2.4 (2)	9.2	–	–	1
p-cymene	1252	tr[c]	tr	–	–	–	–	–	–	1
α-terpinolene	1264	4.2 (8)	4.0	4.6 (1)	3.3	–	–	1.5 (11)	4.2	1
α-gurjunene	1511	–	–	3.0 (3)	2.2	–	–	–	–	2
β-caryophyllene	1582	1.1 (18)	1.1	4.2 (5)	3.0	2.9 (7)	11.1	1.4 (8)	4.0	1
α-humulene	1651	0.6 (11)	0.6	2.1 (6)	1.5	1.5 (3)	5.7	0.7 (8)	2.0	1
β-selinene	1700	5.9 (4)	5.7	9.3 (4)	6.7	–	–	0.7 (24)	2.0	2

[a] Linear retention index. [b] Values in parentheses are coefficients of variation. [c] tr, traces (<50 μg/kg or $<0.1\%$). [d] Not detected. [e] Key for reliability of identification: 1 = linear retention index and mass spectrum of reference compounds; 2 = linear retention index and mass spectrum identical to published data.

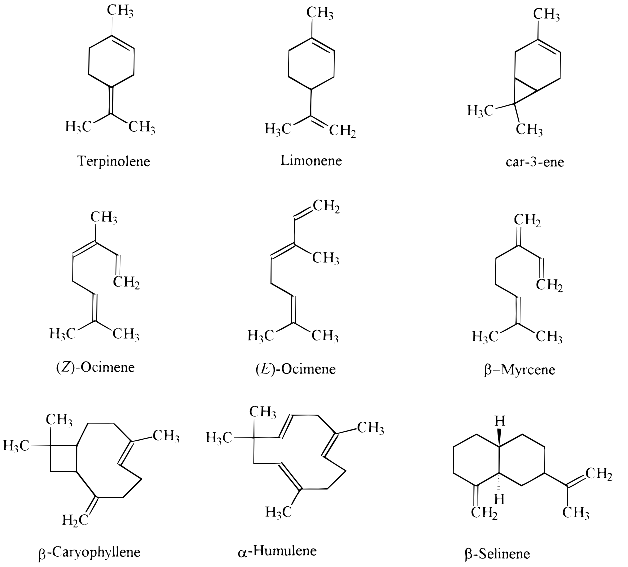

Figure 1. Structures of some mono- and sesquiterpenes of mango.

genated compounds, after adsorption chromatography on Amberlite XAD-2 of model mixtures of alcohols and their glycosides, were previously determined by Voirin et al. (1992), and our results are presented as octan-2-ol equivalents as described above.

Terpene hydrocarbons (Table 1; Figure 1), as in most previously studied mango cultivars (MacLeod and de Troconis, 1982; Engel and Tressl, 1983a; MacLeod and Snyder, 1985, 1988; Schreier and Idstein, 1985; Pino et al., 1989), were by far the dominant volatiles in the studied cultivars, accounting for >90% of total free volatiles (Tables 1 and 2). Apart from the terpene-rich Smith monoembryonic cultivar (~240 mg/kg; Ollé et al., 1997), M'Bingué and Tête de Chat have the highest terpene contents (~100–140 mg/kg) of the previously studied cultivars [e.g. Engel and Tressl (1983a), Schreier and Idstein (1985), and MacLeod and Snyder (1988), while Amélie and Palmer, which have a much milder aroma, are found among the weakly terpenic cultivars (~30–35 mg/kg). Nineteen terpenes were identified, comprising 15 monoterpenes and 4 sesquiterpenes, all of which have been previously reported in mango (TNO, 1996). In all cultivars, except Amélie, car-3-ene was the dominant terpene, accounting for ~75–80% of total terpene hydrocarbons. Other terpenes present in noticeable proportions were α-terpinolene, limonene, α-phellandrene, *β*-myrcene, and *β*-caryophyllene. The two polyembryonic cultivars, M'Bingué and Tête de Chat, exhibited very similar concentrations and qualitative distributions in monoterpenes but not in sesquiterpenes. It is worth mentioning that mono- and sesquiterpene biosyntheses in the calamondin (*Citrofortunella mitis*) are known to occur in different cell compartments, namely leucoplasts and endoplasmic reticulum (Belingheri et al., 1989). The sesquiterpene *β*-selinene was detected in significant amounts in these two polyembryonic cultivars. Furthermore, the monoterpene relative distributions in the studied cultivars, except Amélie, were surprisingly similar and almost identical to the distributions observed in cv. Keitt (MacLeod and Snyder, 1985) and Smith (Ollé et al., 1997) at full ripeness. The (*β*-caryophyllene/α-humulene) ratio was constant (~2) for all studied cultivars and similar to those observed in the headspace of cv. Governor, Peach, Papaya, and Muskat (Koulibaly et al., 1992), in SDE extracts from ripe cv. Tommy Atkins and Keitt (MacLeod and Snyder, 1985), from cv. Alphonso and Baladi (Engel and Tressl, 1983a; Schreier and Idstein, 1985), and in a pentane extract from cv. Smith (Ollé et al., 1997). These two sesquiterpenes were also synthesized in the same ratio by isolated endoplasmic reticulum from maritime pine primary leaves (Gleizes et al., 1980).

Cv. Amélie was distinct from others by being almost devoid of car-3-ene and having (*Z*)- and (*E*)-ocimene as its major monoterpenes. These two latter volatiles have warm, herbaceous, and floral odor, while the odor of car-3-ene is sweet, reminiscent of refined limonene (Arctander, 1969a,b). These aroma characteristics were also observed in canned puree (Hunter et al., 1974), in green and ripe fruits from the Indian cv. Alphonso (Gholap and Bandyopadhyay, 1977; Schreier and Idstein, 1985), and also in the Sri Lankan cv. Jaffna, which is grown in the north of Sri Lanka (MacLeod and Pieris, 1984).

In total, 66 free oxygenated volatile components were detected (Table 2), 60 being positively or tentatively identified by comparison of the GC and GC/MS data with those of reference compounds or with the litera-

Table 2. Distribution of Free Oxygenated Volatile Components (Micrograms per Kilogram) in Cultivars M'Bingué, Tête de Chat, Amélie, and Palmer

compound	LRI[b]	M'Bingué	Tête de Chat	Amélie	Palmer	reliability of ID[f]
monoterpenoids						
neral	1632	−[e]	−	tr	−	1
menthadien-8-ol (isomer 1)[a]	1685	33 (55)[c]	314 (23)	−	24 (20)	2
menthadien-8-ol (isomer 2)[a]	1694	tr[d]	485 (22)	−	22 (24)	2
geranial	1705	−	−	11 (20)	−	1
car-3-en-5-one[a]	1714	10 (39)	79 (9)	−	42 (22)	3
m-cymen-8-ol[a]	1804	tr	71 (35)	−	−	2
p-cymen-8-ol	1809	39 (26)	215 (23)	−	−	2
geraniol	1822	−	tr	−	119 (14)	1
menthadien-7-ol[a]	1908	35 (16)	156 (22)	−	−	3
menthadien-9-ol (isomer 1)[a]	1923			tr		3
menthadien-9-ol (isomer 2)[a]	1949	−	−	14 (29)	−	3
terpenol (isomer 1)[a]	1955	−	−	39 (31)	−	
terpenol (isomer 2)[a]	1994	−	−	225 (26)	−	
carane-3,4-diol[a]	2170	−	393 (19)	−	−	3
8-hydroxylinalool[a]	2251	−	50 (25)	−	−	1
4-hydroxymenthofuran[a]	2392	−	148 (32)	−	−	3
menthadien-7,8-diol (isomer 1)[a]	2482	−	96 (42)	−	−	3
menthadien-7,8-diol (isomer 2)[a]	2495	−	154 (23)	−	−	3
alcohols and aldehydes						
hexanal	1090	tr	−	18 (25)	15 (23)	1
pentan-2-ol	1105	15 (32)	−	tr	15 (15)	1
hexan-2-ol[a]	1159	−	−	tr	21 (19)	2
isoamyl alcohol	1197	−	−	56 (21)	65 (6)	1
(*E*)-hex-2-enal	1209	−	211 (5)	−	32 (21)	1
pent-2-en-1-ol	1315	28 (17)	−	−	44 (25)	1
hexan-1-ol	1349	−	53 (16)	28 (18)	tr	1
(*Z*)-hex-3-en-1-ol	1357	−	123 (22)	41 (15)	86 (14)	1
2-butoxyethanol[a]	1379	−	−	14 (17)	14 (31)	2
heptan-1-ol[a]	1421	−	−	−	tr	2
2,6-nonadienal	1473	−	−	−	181 (47)	2
benzyl alcohol	1828	21 (6)	39 (17)	67 (21)	68 (4)	1
2-phenoxyethanol[a]	2087	28 (1)	−	−	−	2
lactones						
γ-caprolactone	1665	−	−	−	245 (8)	2
δ-caprolactone	1751	−	−	−	84 (6)	2
γ-octalactone + 2-phenylethanol	1866	38 (11)	54 (23)	85 (10)	361 (21)	1
δ-nonalactone	1923	−	−	−	54 (13)	2
phenols and phenol derivatives						
guaiacol[a]	1771	−	18 (15)	−	−	1
creosol[a]	1884	−	16 (24)	−	−	2
phenol + *o*-cresol	1956	15 (14)	87 (19)	−	−	1
eugenol[a]	2117	34 (15)	−	28 (25)	−	1
4-vinylguaiacol[a]	2136	−	−	−	127 (41)	1
propiovanillone[a]	2620	−	−	45 (16)	−	2
zingerone[a]	2716	−	74 (35)	−	−	1
syringaldehyde[a]	2835	14 (24)	−	−	−	1
guaiacylpropanol[a]	2850	215 (27)	−	−	−	2
4-hydroxyacetophenone[a]	2855	40 (33)	−	−	−	2
syringic acid[a]	2867	−	96 (24)	−	−	1
acids						
2-ethylhexanoic acid	1914	23 (12)	−	−	−	2
caprylic acid	2033	26 (20)	−	−	−	1
capric acid	2246	27 (11)	−	22 (65)	−	1
lauric acid	2447	109 (21)	393 (19)	44 (14)	−	1
myristic acid	2656	133 (23)	3919 (15)	90 (14)	488 (21)	1
palmitic acid	2842	859 (28)	3629 (19)	2681 (30)	5472 (8)	1
C_{13} norisoprenoids						
3-oxo-α-ionol[a]	2608	117 (15)	31 (69)	29 (9)	114 (12)	1
3-oxoretro-7,8-dehydro-α-ionol[a]	2630	−	34 (18)	165 (22)	154 (16)	2
3-oxo-7,8-dihydro-α-ionol[a]	2645	40 (26)	97 (27)	197 (11)	540 (11)	2
3-oxoretro-α-ionol (isomer 1)[a]	2660	−	295 (25)	126 (16)	49 (29)	2
3-oxoretro-α-ionol (isomer 2)[a]	2829	−	147 (41)	−	377 (18)	2
vomifoliol[a]	3170	63 (10)	109 (19)	54 (48)	122 (8)	2
7,8-dihydrovomifoliol[a]	3253	−	−	−	tr	2
miscellaneous						
mesifuran	1556	142 (14)	368 (34)	216 (13)	24 (18)	1
unknown 2	1599	−	318 (29)	−	−	
unknown 3 (long chain molecule)	1993	61 (15)	−	535 (18)	566 (17)	
unknown 4 (long chain molecule)	2023	222 (34)	−	539 (32)	102 (41)	
unknown 5 (MW 198)	2832	60 (15)	−	−	32 (48)	

[a] Identified for the first time in mango volatiles. [b] Linear retention index. [c] Values in parentheses are coefficients of variation. [d] tr = traces (<10 μg/kg). [e] Not detected. [f] Key for reliability of identification: 1 = linear retention index and mass spectrum of reference compounds; 2 = linear retention index and mass spectrum identical to published data; 3 = mass spectrum identical with published data.

Table 3. Distribution of Glycosidically Linked Volatile Components (Micrograms per Kilogram) in Cultivars M'Bingué, Tête de Chat, Amélie, and Palmer

compound	LRI[b]	M'Bingué	Tête de Chat	Amélie	Palmer	reliability of ID[f]
monoterpenoids						
menthadien-8-ol (isomer 1)[a]	1685	tr	37 (15)[c]	–[e]	–	2
menthadien-8-ol (isomer 2)[a]	1694	tr	30 (13)	–	–	2
m-cymen-8-ol[a]	1804	–	tr[d]	tr	–	2
p-cymen-8-ol	1809	–	18 (21)	tr	–	2
geraniol[a]	1822	tr	48 (13)	–	–	1
menthadien-7-ol	1908	136 (13)	406 (15)	–	–	3
menthadien-9-ol (isomer 1)[a]	1923	–	–	tr	–	3
menthadien-9-ol (isomer 2)[a]	1949	–	–	21 (47)	–	3
terpenol (isomer 1)	1955	–	–	21 (21)	–	
perillyl alcohol	1962	tr	51 (19)	–	–	1
terpenol (isomer 2)	1994	–	–	89 (15)	–	
carane-3,4-diol[a]	2170	–	49 (23)	–	–	3
8-hydroxylinalool[a]	2251	tr	61 (14)	–	–	1
4-hydroxymenthofuran[a]	2392	–	236 (11)	–	–	3
menthadien-7,8-diol (isomer 1)[a]	2482	tr	87 (13)	tr	–	3
menthadien-7,8-diol (isomer 2)[a]	2495	14 (28)	89 (3)	26 (36)	–	3
acids						
myristic acid	2656	–	152 (42)	–	–	1
palmitic acid	2842	63 (28)	47 (16)	48 (27)	–	1
C_{13} norisoprenoids						
3-oxo-α-ionol	2608	14 (12)	11 (29)	–	23 (32)	1
3-oxoretro-7,8-dehydro-α-ionol	2630	10 (23)	28 (21)	–	–	2
3-oxo-7,8-dihydro-α-ionol	2645	11 (37)	61 (28)	–	50 (24)	2
3-oxoretro-α-ionol (isomer 1)	2660	–	73 (12)	tr	tr	2
3-oxoretro-α-ionol (isomer 2)	2829	–	36 (25)	tr	28 (19)	2
vomifoliol	3170	–	36 (31)	tr	83 (12)	2
7,8-dihydrovomifoliol[a]	3253	–	205 (23)	tr	90 (22)	2
miscellaneous						
benzyl alcohol	1828	179 (3)	275 (13)	24 (36)	55 (4)	2
2-phenylethanol	1866	42 (14)	39 (4)	22 (25)	52 (23)	1
phenol + *o*-cresol	1956	–	28 (12)	24 (24)	–	1

[a] Identified for the first time in glycosidically linked volatile components of mango. [b] Linear retention index. [c] Values in parentheses are coefficients of variation. [d] tr, traces ($<$10 μg/kg). [e] Not detected. [f] Key for reliability of identification: 1 = linear retention index and mass spectrum of reference compounds; 2 = linear retention index and mass spectrum identical to published data; 3 = mass spectrum identical with published data.

ture. About half of these compounds, all of them being hydroxylated, were also found as their nonvolatile precursors (Table 3). The total amounts of free oxygenated volatiles in the different cultivars were as follows: M'Bingué, ~2.4 mg/kg; Amélie, 5.4 mg/kg; Palmer 9.7 mg/kg; and Tête de Chat, 12.3 mg/kg fresh pulp. The total amounts of bound oxygenated volatiles were as follows: Amélie, ~0.3 mg/kg; Palmer, 0.4 mg/kg; M'Bingué 0.5 mg/kg; and Tête de Chat, 2.1 mg/kg fresh pulp. The African cv. Tête de Chat was the richest in both classes of compounds.

Eighteen monoterpenoids were detected as free volatile compounds, most of them being also found as their glycosides. They were mostly observed at their highest levels in cv. Tête de Chat (total concentration: free, ~2 mg/kg; bound, ~0.9 mg/kg). Some menthane-based compounds were tentatively identified. Menthadien-8-ol and menthadiene-7,8-diol were found for the first time as free and bound mango volatiles. A menthadien-7-ol was found only in the two polyembryonic cultivars, and its linear retention index (1908) was different from that of another menthadien-7-ol, the perillyl alcohol (linear retention index = 1962), also found in these cultivars as a bound volatile. It was also reported as a bound volatile component in an unknown polyembryonic African cultivar (Sakho et al., 1997). Two isomers of a menthadien-9-ol were found only in cv. Amélie. Two isomers of an unknown terpenol (MW 152) with linear retention indices of 1955 and 1994 were also exclusively detected in cv. Amélie as free and bound forms and were the major oxygenated terpene of this cultivar. Their mass spectra are shown in Figure 2.

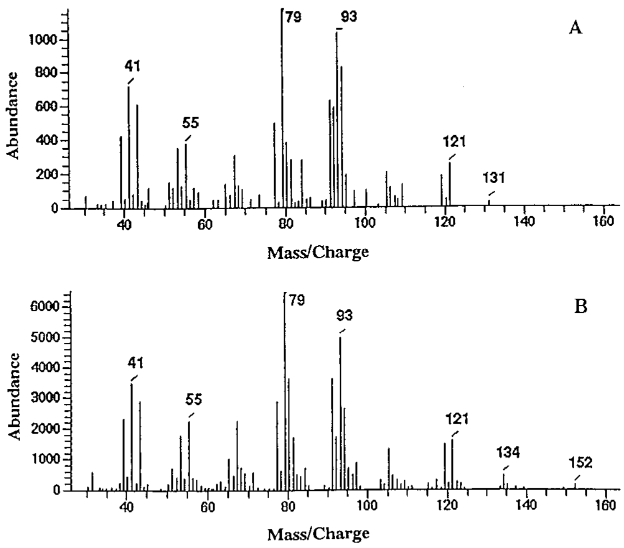

Figure 2. EI mass spectra of two isomers [respective linear retention indices 1955 (A) and 1994 (B)] of an unknown terpenol].

8-Hydroxylinalool, formerly detected as its bound precursor in passion fruit juice (Winterhalter, 1990), was identified for the first time in mango as both free and bound forms. The unique occurrence of geraniol and the absence of linalool, linalool oxides, and other monoterpene alcohols points out the gentleness of the isolation procedure in comparison with simultaneous distillation–extraction which, as demonstrated by Engel and Tressl (1983b), when applied to unbuffered acidic fruit juices (e.g. pulp of the cv. M'Bingué has a pH of 4.2; Ollé et al., 1996), could generate these volatile components.

Of the eight C_{13} norisoprenoids identified, none have been previously described as free volatile components of mango. As already reported in two unknown African cultivars (Adedeji et al., 1992; Sakho et al., 1997), 3-oxo-α-ionol, 3-oxoretro-7,8-dehydro-α-ionol, 3-oxo-7,8-dihydro-α-ionol, 3-oxoretro-α-ionol, and vomifoliol were also found as glycosidically linked aglycons (Table 3). These components were mostly encountered in cv. Palmer and Tête de Chat (total concentration: free, ∼1.4 and 0.7 mg/kg, respectively; bound, ∼0.3 and 0.4 mg/kg, respectively). If these compounds play a significant role in the overall aroma of these cultivars, then the low terpene hydrocarbon content of cv. Palmer might be an indication of their odor potency. Considering the balance between bound and free forms, it is unlikely that glycosidically bound C_{13} norisoprenoids would, if the aglycons were to be released by thermal and enzymatic means, influence the aroma and flavor of the considered cultivars.

Alcohols, aldehydes, and lactones were mainly found in the commercial cv. Palmer. Although γ-octalactone coeluted with 2-phenylethanol, mass fragmentography focused on the peak enabled us to show that the lactone largely predominates in cv. Palmer, whereas these two compounds were found in roughly equivalent proportions in other cultivars.

Contrary to most mango cultivars, esters were not detected under our experimental conditions ($<10\ \mu$g/kg) in any of the cultivars under consideration. However, the presence of esters in mango flesh does not seem to be a general characteristic since they were not detected in a Venezuelan cultivar and in cv. Tommy Atkins (MacLeod and de Troconis, 1982; MacLeod and Snyder, 1985).

Phenols and phenol derivatives were mainly encountered as free compounds in the two African cultivars (∼300 μg/kg), most of them being described for the first time as mango volatile components (Table 1). Only phenol and *o*-cresol were found in bound forms (Table 2).

Free acids (2-ethylhexanoic, caprylic, capric, lauric, myristic, and palmitic) were detected in the four cultivars, while only myristic and palmitic acids were present as their bound forms. Some of these acids were also mentioned in the glycosidically linked fractions from two polyembryonic African cultivars (Adedeji et al., 1992; Sakho et al., 1997).

Mesifuran [2,5-dimethyl-4-methoxy-3(*2H*)-furanone], previously mentioned as a free mango volatile component (Hunter et al., 1974; Engel and Tressl, 1983a; Idstein and Schreier, 1985), was also found in noticeable proportions (∼150−350 μg/kg) in three of the four studied cultivars. This constituent, described as having a sherry wine-like note (Hunter et al., 1974), has a very low detection threshold (0.03 μg/L in water; Pyysalo et al., 1977). It might therefore contribute significantly to the overall aroma of the studied cultivars. Furaneol [2,5-dimethyl-4-hydroxy-3(*2H*)-furanone], formerly reported as a free (Pickenhagen et al., 1981; Schreier and Idstein, 1985) and bound (Sakho et al., 1997) mango volatile compound, was not detected in our study.

CONCLUSION

We have studied free and glycosidically linked volatile components of four mango cultivars. A rapid method has been developed for direct extraction of terpene hydrocarbons, which showed high concentrations of these compounds in the two polyembryonic cultivars and a different composition for the cultivar Amélie. For oxygenated compounds, greater differences were observed between cultivars. Monoterpenoids and C_{13} norisoprenoids were found in higher concentrations, respectively, in cv. Tête de Chat and Palmer. Some of the oxygenated components were also found in bound form. Further studies need to be carried out to study the real impact of monoterpenoids and C_{13} norisoprenoids on the overall aroma of each mango cultivar.

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