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VOLATILE CONSTITUENTS OF ALPHONSO MANGO (*MANGIFERA INDICA*)

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

Abstract—Concentrates of fresh, ripe Indian Alphonso mango fruit were analysed by HRGC and HRGC/MS. In total, 152 aroma substances were identified, of which 70 are reported for the first time as mango fruit constituents. Quantitative HRGC revealed a considerable quantity of aroma compounds (*ca* 57 mg/kg fresh fruit pulp), of which 90% consisted of mono- and sesqui-terpene hydrocarbons. Major constituents included (*Z*)-(44 mg/kg) and (*E*)-ocimene (3 mg/kg) and 2,5-dimethyl-4-hydroxy-3(2H)-furanone (2 mg/kg).

INTRODUCTION

Mango (*Mangifera indica* L.) is one of the most important commercial crops of the world. The fruits from the several hundred known cultivars differ greatly in their flavour characteristics [1–5]. In particular, terpenes [5–7] and esters [4] seem to occur in cultivar typical combinations. Studies on the Alphonso cultivar are rather scarce [2, 4, 6] and some of them have been carried out on canned [8] or unripe fruits [9]. Considering the widespread importance of this cultivar, it was regarded as appropriate to study extensively the aroma substances of the fresh, ripe fruit. This paper describes the results of our study on fruits grown in India.

RESULTS AND DISCUSSION

Aroma concentrates of fresh Alphonso mango fruit were obtained using previously described methods [10]. Their constituents were identified by HRGC and HRGC/MS. Table 1 lists the aroma substances of fresh fruit pulp together with MS data of the separated peaks. Identifications were carried out by comparing the chromatographic and spectroscopic data with those of authentic reference samples. In total, 152 aroma components were identified; of which 70 were newly identified as mango fruit constituents.

The quantitative distribution of the major constituents is given in Table 2. The total amount of aroma compounds was determined to be 57 mg/kg fresh fruit pulp, of which 90% consisted of mono-and sesqui-terpene hydrocarbons. The components listed in Table 1 and not represented in Table 2 were found in amounts $< 50\ \mu g/kg$ fresh fruit pulp.

Hydrocarbons occupy a special place among the volatiles. Qualitatively, with 46 identified substances, they make an important contribution to the complex aroma composition. They are believed to be responsible for the characteristic flavours of certain mango cultivars [2, 5, 9], as their amounts vary strongly with cultivar. In Alphonso mango, the monoterpene hydrocarbons mainly consist of (*Z*)- and (*E*)-ocimene, while, e.g. car-3-ene, a major constituent of Venezuelan mango [5], only occurs in traces. Conversely, β-myrcene found in Alphonso in relatively high amounts, could not be detected in Venezuelan fruit [5]. α-Hymentherene, newly found as a mango constituent, is of particular interest, as it may be involved in the biogenesis of the ocimenes. The possible biogenetic pathways have been discussed elsewhere [11].

Among the esters identified, C_2 and C_4 moieties dominate, i.e. the main part consists of acetates, butanoates or ethyl and butyl esters. In addition to several newly detected terpene esters (acetates and butanoates of menthol, linalool, citronellol and α-terpineol), two formates were identified for the first time in mango. Esters of this type are rarely found in nature [12, 13]. The esters of branched-chain acids can be derived from amino acid metabolism. They mainly comprise saturated and unsaturated esters with isobutyl (methacryl)- and 2-methylbutyl (tiglate) residues. Butyl 2-methacrylate has been found only in tropical beli fruit [14], and, e.g. the tiglates have been seldom identified among plant volatiles [15]. Engel and Tressl [4] found a strong variation of esters with cultivar as well as a characteristic content of (*Z*)-hex-3-enyl esters and a lack of certain ethyl esters in Alphonso cultivar grown in Egypt. The latter results were confirmed by our studies.

Quantitatively, the carbonyls do not play a decisive role among the volatiles; they were mostly determined in amounts $< 50\ \mu g/kg$ fruit pulp. A series of lipid peroxidation products was identified with (*E*,*Z*)-nona-2,6-dienal as major compound (25 μg/kg fruit pulp). The relationship between the formation of mango flavour and the composition of lipids have been discussed [16, 17]. The major constituent among the ketones was 2,5-dimethyl-4-hydroxy-3-(2H)-furanone. As a non-distillable compound, it was only detectable in the residues of high-vacuum distillation of fruit pulp. The amount present (2 mg/kg fresh fruit pulp) is much higher than the amount previously established in an Israeli cultivar [18]. Another group of ketones comprises norcarotenoids, i.e. biodegradation products of carotenoids [19]. This is not unexpected as this fruit is known to be rich in these flavour precursors [20]. The importance of the newly detected 3,7-dimethyl-octa-1,6-dien-4-one has been pointed out elsewhere [11]. The substance might be regarded as a biogenetic intermediate of ocimenes and β-hymentherene.

Similar to the carbonyls, among the alcohols two

Table 1. Aroma compounds identified in Alphonso mango fruit pulp by HRGC and HRGC/MS

Compound	Identified in*	Mass spectral data† (m/z)
Hydrocarbons		
Undecane‡	I	43–41–57–42
Dodecane‡	I	57–43–71–41
Tridecane‡	I	57–43–71–41
Tetradecane	I	57–71–43–85
Pentadecane‡	I	57–71–43–41
Hexadecane	I	57–43–71–41
Heptadecane	I	57–43–41–71
Octadecane	I	57–43–41–71
Nonadecane	I	57–43–41–71
Eicosane	I	57–43–41–71
Heneicosane	I	57–43–41–71
Toluene	I	91–**92**–65–51
Ethylbenzene‡	I	91–**106**–51–65
p-Xylene‡	I	91–**106**–51–105
m-Xylene‡	I	91–**106**–51–105
o-Xylene‡	I	91–**106**–105–51
p-Cymene	I	119–91–**134**–65
Propylbenzene‡	I	91–**120**–65–92
Naphthalene	I	**128**–127–51–129
α-Pinene	I	93–91–41–77
Camphene	I	93–41–79–67
Car-3-ene	I	93–91–41–77
Sabinene‡	I	93–77–79–41
β-Myrcene	I	41–69–93–91
Limonene	I	68–67–93–41
(*Z*)-Ocimene	I	93–41–79–91
(*E*)-Ocimene	I	93–41–79–91
γ-Terpinene	I	93–91–77–121
Terpinolene	I	93–121–**136**–91
(*Z*)-Alloocimene (int. standard)	I	121–105–79–91
α-Hymentherene‡	I	81–79–53–41
α-Caryophyllene	I	93–80–41–121
β-Caryophyllene	I	41–69–93–79
δ-Cadinene	I	161–134–119–105
Esters		
3-Methylbutyl formate‡	III	55–70–43–42
(*Z*)-Hex-3-enyl formate‡	III	57–41–82–55
Ethyl acetate	II	43–61–45–70
Butyl acetate	II	43–56–41–61
2-Methylbutyl acetate	II	43–70–55–73
3-Methylbutyl acetate	II	43–70–55–42
(*Z*)-Hex-3-enyl acetate	II/III	67–43–82–41
2-Phenethyl acetate	II	43–104–91–65
Citronellyl acetate	II	43–41–69–81
Menthyl acetate‡	II	43–95–81–41
Linalyl acetate	II	43–71–41–55
Neryl acetate‡	II/III	59–43–41–93
Ethyl methacrylate‡	II	41–69–99–68
Butyl methacrylate‡	II	41–69–87–56
Ethyl butanoate	II	43–71–88–41
Methylpropyl butanoate	II	71–43–56–41
Butyl butanoate	II	71–56–43–89
3-Methylbutyl butanoate	II	43–71–70–55
Hexyl butanoate	II	56–43–71–89
(*Z*)-Hex-3-enyl butanoate	II	57–43–71–82
2-Phenethyl butanoate‡	II	104–43–71–91
Neryl butanoate‡	II	59–93–80–58
Terpinyl butanoate‡	II	121–93–71–136
Butyl (*E*)-but-2-enoate‡	II	69–41–87–56
(*Z*)-Hex-3-enyl (*E*)-but-2-enoate	II	69–67–82–41
Ethyl 2-methylbutanoate‡	II	57–41–102–85
Butyl tiglate‡	II	55–101–83–56
Butyl hexanoate	II	56–99–43–117
(*Z*)-Hex-3-enyl hexanoate	II	67–82–43–41
Methyl phenylacetate (int. standard)	II	91–**150**–65–59
Ethyl phenylacetate‡	II	91–**164**–92–65
Methyl benzoate‡	II	105–77–51–**136**
Carbonyls		
But-2-enal	III	41–**70**–69–44
3-Methylbutanal‡	II	41–44–43–58
(*E*)-Pent-2-enal	III	55–83–41–**84**
2-Methyl-pent-2-enal	III	41–**98**–69–55
Hexanal	II	44–43–41–56
(*E*)-Hex-2-enal	II/III	41–55–69–42
(*E,E*)-Hexa-2,4-dienal‡	III	81–41–53–**96**
Heptanal‡	II	44–43–42–41
(*E,E*)-Hepta-2,4-dienal‡	III	81–41–53–**110**
Octanal	II	43–44–42–41
Nonanal	II	41–43–44–57
(*E,E*)-Nona-2,6-dienal‡	II	41–69–70–43
(*E,Z*)-Nona-2,6-dienal	II	41–70–69–43
(*Z-E*)-Nona-2,6-dienal‡	II	41–70–69–43
Decanal‡	II	41–43–57–44
Dodecanal‡	II	43–41–57–55
Benzaldehyde	II	77–105–**106**–51
Phenylacetaldehyde	II/III	91–65–92–**120**
3-Furancarboxaldehyde‡	III	41–67–65–51
5-Methylfurfural	III	109–**110**–53–81
Neral‡	III	41–69–53–91
Geranial‡	III	41–69–93–55
Butandione‡	III	43–**86**–58–71
3-Hydroxy-butan-2-one	III	45–43–**88**–42
Pentan-3-one	II	57–43–**86**–58
Pent-3-en-2-one	II/III	41–69–43–**84**
Hexan-3-one‡	II	43–57–71–**100**
3,5,5-Trimethylcyclohex-2-en-1-one‡	III	82–54–41–**138**
Cyclohexanone‡	II	55–42–**98**–41
Heptan-3-one	II	57–85–41–72
6-Methyl-hept-5-en-2-one‡	II	43–41–55–69
3,7-Dimethyl-octa-1,6-dien-4-one‡	II	69–41–55–53
Acetophenone	II	77–105–51–**120**
Geranylacetone‡	II	43–69–41–93
Acetylfuran‡	III	95–**110**–43–67
2,5-Dimethyl-4-methoxy-3(2H)-furanone	III	43–**142**–55–41
2,5-Dimethyl-4-hydroxy-(2H)-furanone	R	43–**128**–57–85
Alcohols		
2-Methyl-propan-1-ol	III	43–42–41–**74**
Butan-1-ol	III	56–41–43–42
Butan-2-ol	III	43–53–59–41
3-Methyl-butan-1-ol	III	55–42–41–43
Pentan-1-ol	III	42–41–55–70
Pentan-2-ol	III	45–55–43–42
Pentan-3-ol‡	III	59–41–57–58
(*Z*)-Pent-2-en-1-ol‡	III	57–41–67–68
Pent-1-en-3-ol‡	III	57–67–58–68
Hexan-1-ol	III	56–43–41–55
Hexan-3-ol‡	III	41–67–55–42

Table 1. (*Continued*)

Compound	Identified in*	Mass spectral data† (m/z)
(E)-Hex-3-en-1-ol	III	41–67–55–42
(E)-Hex-2-en-1-ol	III	57–41–67–82
2-Ethyl-hexan-1-ol‡	III	57–43–41–55
Octan-1-ol‡	III	56–41–55–43
2,7-Dimethyl-octan-1-ol‡	III	55–43–41–56
Decan-1-ol‡	III	43–41–55–56
Undecan-1-ol (int. standard)	III	43–41–55–56
Dodecan-1-ol‡	III	43–41–55–56
Tetradecan-1-ol‡	III	43–55–57–41
Pentadecan-1-ol‡	III	43–57–55–41
Hexadecan-1-ol	III	43–57–55–41
Heptadecan-1-ol‡	III	43–57–55–41
Octadecan-1-ol‡	III	43–57–55–41
Tetrahydrofurfuryl alcohol‡	III	71–43–41–42
Linalool	II/III	71–41–43–55
Geraniol‡	III	69–41–93–68
Menthol‡	III	
Dihydrocarveol‡	III	41–43–55–93
Lactones		
γ-Butyrolactone	III	42–41–**86**–56
2-Methyl-γ-butyrolactone	III	41–56–42–**100**
γ-Valerolactone‡	III	42–56–71–**100**
γ-Hexalactone	III	85–57–56–42
δ-Hexalactone‡	III	42–43–70–55
γ-Heptalactone	III	85–56–41–43
γ-Octalactone	III	85–57–41–56
δ-Octalactone	III	42–99–55–41
γ-Nonalactone	III	85–57–41–55
δ-Nonalactone‡	III	42–99–41–55
γ-Decalactone	III/R	85–41–55–57
δ-Decalactone	III/R	99–42–71–55
(Z)-Jasmolactone‡	R	71–99–55–43
γ-Dodecalactone‡	R	85–56–55–57
Miscellaneous		
Acetic acid	III	43–45–60–42
Hexanoic acid‡	III/R	60–73–41–43
Octanoic acid	III/R	60–73–41–43
Phenol‡	III	**94**–66–65–63
Benzothiazol	III	**135**–108–69–63
(Z)-Linalool oxide, furanoid	III	59–43–94–55
(E)-Linalool oxide, furanoid	III	59–43–94–55
1,8-Cineol‡	II	43–81–71–93
8,8-Dimethyl-2-methylene-6-oxabicyclo [3.2.1]octane‡	II	107–41–79–121

*I–III: silica gel fractions; R: residues of high-vacuum distillation.

†The four most abundant peaks are represented (M^+ in bold).

‡Reported for the first time as mango fruit constituent.

principal biogenetic pathways can be considered, i.e. amino acid metabolism leading to volatiles such as butan-1-ol, 2-methyl-propan-1-ol or 3-methyl-butan-1-ol and the lipid peroxidation pathways giving rise to C_5 and C_6 unsaturated alcohols. Furthermore, several terpene alcohols of different oxidation state were found. Thus, in addition to the well-known linalool, saturated compounds such as menthol or 2,7-dimethyl-octan-1-ol were found for the first time as mango constituents.

The most comprehensive range of lactones described as yet among plant volatiles was detected. Even in fruits such as apricot [21], peach [22] or coconut [23], in which lactones are key flavour constituents, such a complexity of lactones is not found. Among fourteen identified γ- and δ-lactones, five of these compounds are described for the first time as mango fruit constituents including (Z)-jasmolactone, a compound known to be present in black tea aroma [24]. The corresponding free acid, in its (Z)- and (E)-configuration was also be found in our study on volatile acids [25], thus confirming the postulated biogenetic pathway of lactones via their hydroxy acids [21, 26].

In the group of compounds with miscellaneous structures several ethers were newly identified as mango fruit constituents, among them the structurally interesting 8,8-dimethyl-2-methylene-6-oxabicyclo[3.2.1]octane (karahanaether), first detected in Japanese hop oil [27].

EXPERIMENTAL

Sample preparation. Fresh, ripe Alphonso mangoes were obtained from Sudha Instant Soft Drinks and Essences, Nagpur (India), by air freight and were analyzed the day after arrival. After removal of the skin and the kernel, homogenization by a Waring blendor and separation by a hydraulic press (Hafico) 2.7 kg fresh fruit pulp was obtained from 4.0 kg fruits. Internal standards were added to the pulp (1.0 mg alloocimene; 1.0 mg methyl phenylacetate; 0.95 mg undecan-1-ol). High-vacuum distillation with subsequent solvent extraction (pentane–CH_2Cl_2, 2:1) was carried out as previously described [10]. Non-distillable aroma substances were separated from the distillation residues by direct solvent extraction. After a preliminary fractionation of the carefully concentrated [10] extracts by LC on silica gel using a pentane–Et_2O gradient in three fractions (fraction I, eluted with pentane; fraction II, Et_2O–pentane 1:9; fraction III, Et_2O) [10] samples were concentrated to 0.2 ml before HRGC and HRGC/MS analysis.

HRGC. A 30 m × 0.31 mm i.d. J & W fused silica capillary CW 20 M column (d.f. = 0.15 μm) with a 2 m uncoated fused silica capillary precolumn ('retention gap') [28] was used. On-column injection with an air-cooled injection system was employed. Temp. program, 50–240° at 2°/min. Carrier gas, 2.5 ml He/min; make-up gas 30 ml/min N_2; detector gases, 30 ml/min H_2 and 300 ml/min air. Detector temperature, 220°. Results of qualitative analyses were confirmed by comparison of HRGC retention and mass spectral data which those of authentic reference substances. Quantitative determinations were carried out by standard controlled calculations without consideration of distillation and extraction yields, i.e. calibration factors $F = 1.00$ for all compounds.

HRGC/MS. A Varian Aerograph 1440 equipped with a water-cooled on-column injector coupled by an open split interface to a Finnigan MAT 44 system was used. A MEGA CW 20 M (25 m × 0.32 mm i.d.) fused silica column (d.f. = 1.0 μm) connected to a 2 m uncoated fused silica column [28] was employed. Column temp., 5 min isothermal at 60°, then 60–240° at 2° min. Carrier gas, 2.5 ml/min He. Temp. of ion source and connection parts, 200°. Electron energy, 70 eV. Cathodic current, 0.8 mV. Injection vol., 0.3 μl.

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Table 2. Quantitative distribution of major aroma compounds of Alphonso mango fruit*

Class	Wt. range (μg/kg pulp) 10–50	50–250	250–1250	> 1250
Hydrocarbons				
	Camphene	α-Pinene	β-Myrcene	(E)-Ocimene
	Limonene	α-Caryophyllene	β-Caryophyllene	(Z)-Ocimene
Carbonyls				
	Butandione		3-Hydroxy-butan-2-one	
	(E,Z)-Nona-2,6-dienal			
	3,5,5-Trimethylcyclohex-2-en-1-one			
Esters				
	3-Methylbutyl formate	(Z)-Hex-3-enyl acetate		
	3-Methylbutyl butanoate	2-Phenethyl acetate		
Alcohols				
	Pentan-1-ol	2-Methyl-propan-1-ol	Butan-1-ol	
	Pentan-2-ol	Pent-1-en-3-ol	3-Methyl-butan-1-ol	
	Pentan-3-ol	(E)-Hex-2-en-1-ol	(Z)-Hex-3-en-1-ol	
	Hexan-1-ol	Dodecan-1-ol	Tetradecan-1-ol	
	2-Ethyl-hexan-1-ol	Linalool	Hexadecan-1-ol	
	(E)-Hex-3-en-1-ol	Geraniol		
	Octan-1-ol			
	Menthol			
Lactones				
	2-Methyl-γ-butyrolactone	γ-Valerolactone	γ-Butyrolactone	
	γ-Nonalactone	γ-Heptalactone	γ-Hexalactone	
		γ-Octalactone	δ-Hexalactone	
		γ-Nonalactone	δ-Octalactone	
			γ-Decalactone	
Miscellaneous				
		Benzothiazol	2,5-Dimethyl-4-methoxy-3(2H)-furanone	2.5-Dimethyl-4-hydroxy-3(2H)-furanone
		Phenol		

*Standard controlled capillary GC determinations in fruit pulp without consideration of calibration factors, i.e. $F = 1.00$ for all compounds.

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