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## Studies on the Volatile Components of Two Mango Varieties

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The volatile composition of two mango varieties (Alphonso and Baladi) was investigated by means of standard-controlled distillation-extraction, liquid-solid chromatography, and gas chromatography-mass spectrometry. This combination led to the characterization of a spectrum of 114 components of which 81 were identified for the first time as mango constituents. In addition to this qualitative identification, the concentrations of the components were quantitatively determined in a range from 40 ppm to the ppb trace level. By this method clear differences between the two mango varieties could be demonstrated.

Mango (*Mangifera indica* L.), one representative of the group of tropical fruits, becomes more and more important also on European markets. Although the popularity of mangos is increasing just because of their strong and pleasant aroma, there is only little information about the flavor and aroma components of this fruit.

Angelini et al. (1973) characterized the aromatic principles of ripe mangos as hydrocarbons, esters, alcohols, carbonyls, and lactones. Hunter et al. (1974) investigated

the volatile components of canned Alphonso mango. Bandyopadhyay and Gholap (1973) reported on the relationship of mango aroma to fatty acid composition, and Gholap and Bandyopadhyay (1977) characterized *cis*-ocimene and  $\beta$ -myrcene to be responsible for the typical green aroma of raw mangos. MacLeod and Troconis (1982) described car-3-ene as the major aroma-contributing component in Venezuelan mangos. Besides the well-known variety Alphonso, there is a large number of other varieties cultivated in many tropical areas all over the world. Bandyopadhyay and Gholap (1979), Diaz (1980), and Abd El-Baki et al. (1981) investigated some of these varieties, and they reported on considerable differences in the aromatic principles reaching from woody and camphory to

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almond- and coconut-like notes.

The number of components identified in the previous studies is relatively small compared to those of other fruits. Therefore, in the present work we wanted to develop a method to identify a broader spectrum of mango aroma constituents; besides this qualitative identification we wanted to determine quantitatively the approximate concentration range of the components and to demonstrate by this method the differences between two mango varieties.

#### EXPERIMENTAL SECTION

Two varieties of mango (Alphonso and Baladi) were obtained by air freight from Egyptian local markets. In Egypt Alphonso, a variety known for its strong aroma, is mostly used for direct consumption, whereas Baladi, a cheaper variety, is widely used for commercial juice production. The fruits, showing desirable color, texture, and flavor qualities, arrived in the full ripe state and were analyzed within 24 h (storage at 4 °C).

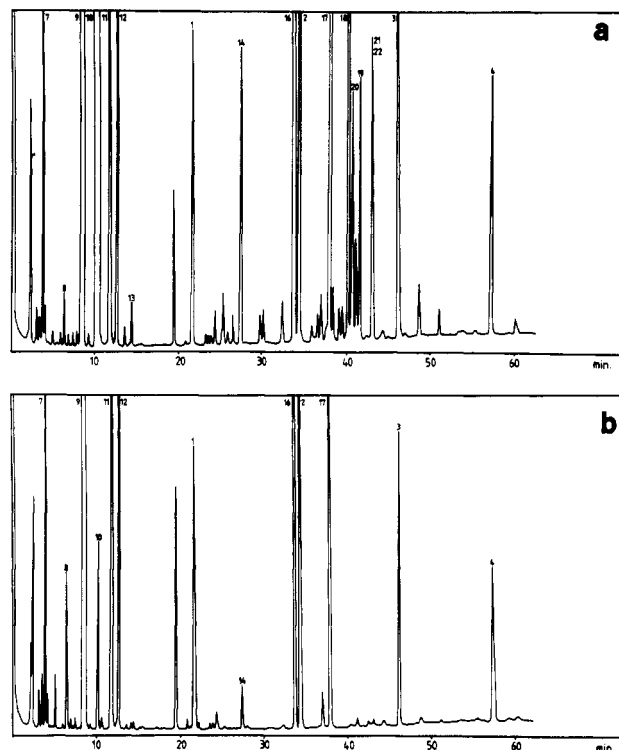
**Sample Preparation.** Three hundred grams of fruit pulp was homogenized with 500 mL of phosphate buffer solution (pH 6.8). A total of 0.3 mg of tridecane and 0.3 mg of 1-heptanol were added as standards, and the volatile constituents were isolated by means of simultaneous distillation-extraction using pentane-ether (1:1) for 2 h (Schultz et al., 1977). The aroma extract was dried over  $\text{Na}_2\text{SO}_4$  and concentrated to a volume of 0.3 mL by using a Vigreux column.

**Adsorption Chromatography.** Separation according to the polarity of the components was carried out by liquid-solid chromatography. The aroma concentrate was placed on a water-cooled column (200 × 9 mm i.d.) filled with 5 g of silica gel (activity II-III, Merck 7734). The hydrocarbons were eluted with 80 mL of (I) pentane and the oxygenated components with 80 mL of ether. Both fractions were concentrated to a definite volume by using a Vigreux column and analyzed by GLC. The oxygenated constituents were separated again into five fractions on silica gel and eluted with 40 mL of (II) pentane-methylene chloride (P-MC) (9:1), (III) P-MC (2:1), (IV) P-MC (1:2), (V) P-ether (9:1), and (VI) ether. The different fractions were concentrated to a volume of 0.3 mL and investigated by GLC and capillary GLC-MS.

**Capillary GLC-Mass Spectrometry.** Capillary GLC was carried out by using a 50-m glass capillary column (0.25-mm i.d.) coated with Carbowax 20M (column A). The column was programmed at 2 °C/min from 70 to 180 °C in a Carlo Erba Fractovap 2900. For capillary GLC-mass spectrometry, a 50-m glass capillary column (0.32-mm i.d.) coated with UCON (column B) was connected to a double-focusing mass spectrometer CH 5-DF (Varian MAT, West Germany). Conditions were as follows: column temperature program 70-180 °C at 2 °C/min (Carlo Erba Fractovap 2101), ionization voltage 70 eV, ion source temperature 200 °C, and the resolution 2000 (10% valley).

**Quantitative Analysis.** Quantitative determinations were carried out by using a computing integrator (SP 4100, Spectra Physics). The calculations were based on the added standards: tridecane for the fraction of hydrocarbons and 1-heptanol for the fraction containing oxygenated components. Calibration factors, related to these internal standards, involving variations in the gas chromatographic response and in the recovery after distillation-extraction and liquid-solid chromatography were determined in model experiments with authentic compounds.

**References.** Reference samples were purchased as much as possible or were gifts from Haarmann and Reimer



**Figure 1.** Gas chromatograms of the LSC fractions containing hydrocarbons: (a) Baladi mango; (b) Alphonso mango (column A; peak numbers correspond to the component numbers in Table I).

(Holzminden), Dragoco (Holzminden), and Firmenich (Geneva).

The newly described esters were synthesized by inter-esterification of the methyl esters of the acids with the corresponding alcohols catalyzed by 4-toluenesulfonic acid.

#### RESULTS AND DISCUSSION

Aroma constituents of two commercial mango varieties, Alphonso and Baladi, were isolated by means of distillation-extraction. The complex mixture of components was separated by liquid-solid chromatography into six fractions according to the polarity of the constituents. Each fraction was examined by GLC and by capillary GLC-mass spectrometry. Distillation-extraction, liquid-solid chromatography (LSC), and gas chromatography were carried out with internal standards. This combination of standardized isolation, LSC, and GLC, GLC-MS made possible the characterization of 114 components, of which 85 were identified for the first time in mango; in addition to this qualitative identification, a quantitative determination of the components in a range from 40 ppm to about 1 ppb was achieved. These results are summarized in Table I. The capillary gas chromatograms (column A) of Alphonso and Baladi mango after separating the aroma concentrates in a fraction of hydrocarbons and a fraction containing the oxygenated components are presented in Figures 1 and 2. It can be seen that there are large qualitative and quantitative differences between the two varieties.

The hydrocarbons myrcene and (*Z*)-ocimene, reported by Gholap and Bandyopadhyay (1977) to be responsible for the green aroma of raw mangos, were contained in both varieties in the same range. On the other hand limonene was the main component (40 ppm) in Baladi mango but was contained in Alphonso only in an amount of 300 ppb.  $\alpha$ -Gurjunene, germacrene D, bicyclogermacrene,  $\gamma$ - and  $\delta$ -cadinene and  $\alpha$ -selinene were identified for the first time in mango. They could only be detected in the variety Baladi but not in Alphonso. In a recent investigation

Table I. Components Identified in Mango

component	$I_K$ (UCON)	LSC	Alphonso approx concn, <sup>e</sup> ppb	Baladi approx concn, <sup>e</sup> ppb	identification
Hydrocarbons					
1, tetradecane	1400	I	250	350	MS <sup>a,b</sup>
2, hexadecane	1600	I	300	500	MS <sup>a,b</sup>
3, octadecane	1800	I	300	600	MS <sup>a,b</sup>
4, eicosane	2000	I	150	300	MS <sup>a,b</sup>
5, benzene	833	II	40	30	MS <sup>a,b</sup>
6, toluene	933	II	50	40	MS <sup>a</sup>
7, $\alpha$ -pinene	982	I	900	800	MS <sup>a</sup>
8, $\beta$ -pinene	1048	I	200	50	MS <sup>a</sup>
9, myrcene	1094	I	19000	17000	MS <sup>a</sup>
10, limonene	1126	I	300	40000	MS <sup>a</sup>
11, ( <i>Z</i> )-ocimene	1156	I	7500	5000	MS <sup>a</sup>
12, ( <i>E</i> )-ocimene	1170	I	1000	1500	MS <sup>a</sup>
13, $\alpha$ -terpinolene	1260	I	5	40	MS <sup>a,b</sup>
14, $\alpha$ -copaene	1437	I	50	800	MS <sup>a,b</sup>
15, $\alpha$ -gurjunene	1467	I		50	MS <sup>a,b</sup>
16, $\beta$ -caryophyllene	1511	I	1400	2300	MS <sup>a</sup>
17, humulene	1570	I	800	1300	MS <sup>a</sup>
18, germacrene D	1605	I		2000	MS <sup>a,b</sup>
19, bicyclogermacrene	1628	I		200	MS <sup>a,b</sup>
20, $\alpha$ -selinene	1615	I		200	MS <sup>a,b</sup>
21, $\gamma$ -cadinene	1647	I		150	MS <sup>a,b</sup>
22, $\delta$ -cadinene	1647	I		150	MS <sup>a,b</sup>
Esters					
23, methyl butanoate	892	II, III		20	MS <sup>a,b</sup>
24, ethyl acetate	887	III, IV	5	500	MS <sup>a</sup>
25, ethyl 2-methylpropanoate	892	II, III		150	MS <sup>a,b</sup>
26, ethyl butanoate	930	II, III	5	8500	MS <sup>a,b</sup>
27, ethyl 3-methylbutanoate	970	III		10	MS <sup>a,b</sup>
28, ethyl hexanoate	1138	II, III		40	MS <sup>a,b</sup>
29, ethyl octanoate	1342	II, III		150	MS <sup>a,b</sup>
30, ethyl decanoate	1542	II, III		80	MS <sup>a</sup>
31, ethyl dodecanoate	1747	II, III	20	200	MS <sup>a</sup>
32, ethyl tetradecanoate	1950	III	30	250	MS <sup>a,b</sup>
33, ethyl hexadecanoate	2150	III	70	100	MS <sup>a,b</sup>
34, butyl acetate	967	III	100	10	MS <sup>a,b</sup>
35, butyl butanoate	1128	III	5	40	MS <sup>a</sup>
36, butyl hexanoate	1328	II		20	MS <sup>a,b</sup>
37, isobutyl acetate	918	III	80	120	MS <sup>a</sup>
38, isobutyl butanoate	1077	II, III	5	50	MS <sup>a</sup>
39, isoamyl acetate	1021	II, III	20		MS <sup>a,b</sup>
40, isoamyl butanoate	1182	II, III		50	MS <sup>a</sup>
41, hexyl acetate	1167	II	200		MS <sup>a,b</sup>
42, hexyl butanoate	1328	II	10	10	MS <sup>a,b</sup>
43, ( <i>Z</i> )-3-hexenyl acetate	1188	III	700	20	MS <sup>a,b</sup>
44, ( <i>E</i> )-3-hexenyl acetate	1194	III	5		MS <sup>a,b</sup>
45, ( <i>E</i> )-2-hexenyl acetate	1211	III	10		MS <sup>a,b</sup>
46, ( <i>Z</i> )-3-hexenyl propanoate	1270	II, III	10		MS <sup>a,b</sup>
47, ( <i>Z</i> )-3-hexenyl butanoate	1350	II, III	30		MS <sup>a,b</sup>
48, 2-phenethyl acetate	1579	IV	20		MS <sup>a,b</sup>
49, 2-phenethyl butanoate <sup>d</sup>	1803	IV	10		MS <sup>b</sup>
50, ( <i>Z</i> )-3-hexenyl butenoate <sup>d</sup>	1403	II	40		MS <sup>b</sup>
51, ( <i>Z</i> )-3-hexenyl ( <i>E</i> )-2-butenate	1453	II	40		MS <sup>b,c</sup>
52, a ( <i>Z</i> )-3-hexenyl pentenoate	1528	II	20		MS <sup>b</sup>
53, ( <i>Z</i> )-3-hexenyl ( <i>E</i> )-2-hexenoate	1638	II	10		MS <sup>b,c</sup>
54, ethyl 3-hydroxybutanoate	1320	VI	50	1500	MS <sup>a,b</sup>
55, ethyl 3-hydroxyhexanoate	1480	VI		50	MS <sup>a,b</sup>
56, butyl 3-hydroxybutanoate	1500	VI		30	MS <sup>b,c</sup>
57, isobutyl 3-hydroxybutanoate	1447	VI		50	MS <sup>b,c</sup>
58, isoamyl 3-hydroxybutanoate	1554	VI		30	MS <sup>b,c</sup>
59, ( <i>Z</i> )-3-hexenyl 3-hydroxybutanoate	1730	VI	20		MS <sup>b,c</sup>
Aldehydes and Ketones					
60, 3-pentanone	858	III		20	MS <sup>a,b</sup>
61, hexanal	967	II, III	100		MS <sup>a,b</sup>
62, ( <i>E</i> )-2-hexenal	1075	IV, V	1000		MS <sup>a,b</sup>
63, a hexenal	1060	IV	30		MS <sup>b</sup>
64, 2-heptanone	1069	IV	100		MS <sup>a,b</sup>
65, ( <i>E</i> )-2-nonenal	1385	IV		50	MS <sup>a,b</sup>
66, ( <i>E,Z</i> )-2,6-nonadienal	1410	IV	50	300	MS <sup>a,b</sup>
67, 2-tridecanone	1684	III	10		MS <sup>a,b</sup>
68, furfural	1217	V	50	20	MS <sup>a</sup>
69, benzaldehyde	1295	III	20		MS <sup>a</sup>
70, phenylacetaldehyde	1392	III, IV	100		MS <sup>a</sup>
71, $\beta$ -cyclocitral	1447	III	10		MS <sup>b</sup>
72, damascenone	1628	V		2	MS <sup>a,b</sup>
73, $\beta$ -ionone	1739	V	10		MS <sup>a</sup>

Table I (Continued)

component	$I_K$ (UCON)	LSC	Alphonso approx concn, <sup>e</sup> ppb	Baladi approx concn, <sup>e</sup> ppb	identification
Alcohols					
74, 1-butanol	1000	VI	100	500	MS <sup>a</sup>
75, 2-butanol	892	VI	10	20	MS <sup>a,b</sup>
76, 2-methylpropan-1-ol	944	VI	500	1000	MS <sup>a,b</sup>
77, 3-methyl-2-buten-1-ol	1147	VI	60	20	MS <sup>a,b</sup>
78, 2-methyl-3-buten-2-ol	892	VI	100	100	MS <sup>a,b</sup>
79, 1-pentanol	1106	VI	10	10	MS <sup>a,b</sup>
80, 2-pentanol	989	VI	30	30	MS <sup>a,b</sup>
81, 3-methylbutan-1-ol	1063	VI	400	250	MS <sup>a</sup>
82, 1-hexanol	1210	VI	1000	50	MS <sup>a,b</sup>
83, ( <i>Z</i> )-3-hexen-1-ol	1220	VI	2500	100	MS <sup>a,b</sup>
84, ( <i>E</i> )-3-hexen-1-ol	1215	VI	10	1	MS <sup>a,b</sup>
85, ( <i>E</i> )-2-hexen-1-ol	1231	VI	50	10	MS <sup>a,b</sup>
86, 1-hexadecanol	2227	VI	500	500	MS
87, 2-phenylethanol	1630	VI	10		MS <sup>a</sup>
88, $\alpha$ -terpineol	1512	VI	5	20	MS <sup>a</sup>
89, $\beta$ -terpineol	1458	VI		100	MS <sup>a,b</sup>
90, linalool	1392	VI	10		MS <sup>a</sup>
91, ( <i>Z</i> )-carveol	1639	VI		10	MS <sup>b</sup>
92, ( <i>E</i> )-carveol	1614	VI		90	MS <sup>b</sup>
Sesquiterpene Epoxides and Alcohols					
93, humulene epoxide I	1833	IV, V	10	20	MS <sup>a,b</sup>
94, humulene epoxide II	1856	IV, V	80	2	MS <sup>a,b</sup>
95, caryophyllene epoxide	1807	IV, V	200	30	MS <sup>a,b</sup>
96, globulol	1877	VI		20	MS <sup>a,b</sup>
97, viridiflorol	1886	VI		20	MS <sup>a,b</sup>
98, cubenol	1881	VI		10	MS <sup>a,b</sup>
99, $\alpha$ -cadinol	2000	V		70	MS <sup>a,b</sup>
100, $\delta$ -cadinol	1953	V		10	MS <sup>a,b</sup>
101, selin-11-en-4-ol	2007	VI		5	MS <sup>a,b</sup>
Lactones					
102, 4-butanolide	1438	VI	50	50	MS <sup>a</sup>
103, 4-pentanolide	1500	VI	20	20	MS <sup>a,b</sup>
104, 4-hexanolide	1540	VI	50	40	MS <sup>a</sup>
105, 4-octanolide	1646	VI	150	500	MS <sup>a</sup>
106, 5-octanolide	1683	VI	30	50	MS <sup>a</sup>
107, 4-nonanolide	1752	VI	30	40	MS <sup>a</sup>
108, 4-decanolide	1863	VI	50	40	MS <sup>a</sup>
109, 5-decanolide	1897	VI	20	40	MS <sup>a,b</sup>
Miscellaneous					
110, acetoin	1085	VI	100	100	MS <sup>a</sup>
111, 2,5-dimethyl-4-methoxy-3(2 <i>H</i> )-furanone	1379	VI	50	150	MS
112, 4-vinylphenol	2000	V	10		MS <sup>a,b</sup>
113, (methylthio)phenaldehyde	1458	III	10		MS <sup>b</sup>
114, benzothiazol	1636	V	10		MS <sup>b</sup>

<sup>a</sup> Comparison of retention time and MS with those of the authentic sample. <sup>b</sup> Identified for the first time in mango.  
<sup>c</sup> Synthesis. <sup>d</sup> See Results and Discussion. <sup>e</sup> Average values of six sample preparations.

Tressl et al. (1983) could characterize these hydrocarbons as constituents of some hop varieties. According to the biogenetical relations and the possible transformations of these hydrocarbons, demonstrated in hop, we could also detect the corresponding oxygenated sesquiterpenoids globulol, viridiflorol, cubenol,  $\alpha$ - and  $\delta$ -cadinol, and selin-11-en-4-ol in Baladi mango. Ledol, the diastereoisomer of viridiflorol, was identified in mango by Diaz (1980).

Large differences between the two varieties can also be seen in the ester fractions. Baladi contains the complete series of ethyl esters of the even-numbered fatty acids from C<sub>2</sub> to C<sub>16</sub> in relatively high amounts; these esters could not be detected or were contained only as trace components in Alphonso mangos. On the other hand (*Z*)-3-hexenyl esters and esters of unsaturated acids were characteristic constituents of the Alphonso mangos investigated in this study. The position and configuration of the double bonds in (*Z*)-3-hexenyl (*E*)-2-butenate and (*Z*)-3-hexenyl (*E*)-2-hexenoate were determined by comparison of mass spectra and retention times with those of synthesized

samples. (*Z*)-3-Hexenyl (*E*)-2-hexenoate has been described previously as a tea constituent by Renold et al. (1974). (*Z*)-3-Hexenyl (*E*)-2-butenate has so far not been identified as a food volatile and possesses a strong fruity, green aroma with an apple-like note. On the basis of their mass spectra (Table II), components no. 49 and 50 were identified as phenethyl and (*Z*)-3-hexenyl butenoates. The position and configuration of the double bond in the acidic moiety of these esters, possessing shorter retention times than the corresponding synthesized (*E*)-2-butenates, could not be determined, because not enough of these materials was isolated to obtain infrared spectra. From a biogenetical point of view the position of the double bond could be in the C<sub>2</sub>- as well as in the C<sub>3</sub>-position, if postulating a biosynthesis of these esters via dehydration of the corresponding esters of 3-hydroxy acids. MacLeod and Pieris (1981) suggested similar relations concerning 3-hydroxy and unsaturated esters in wood apple fruit.

In addition to the lactones, as intramolecular esters of 4- and 5-hydroxy acids, which were characterized in mango

Table II. Mass Spectral and Gas Chromatographic Data of Newly Described Components

component	$I_K$ (UCON)	$I_K$ (CW2OM)	$M_r$	fragmentation, $m/e$ (rel intensity)
51, ( <i>Z</i> )-3-hexenyl ( <i>E</i> )-2-butenate	1453	1585	168	69 (100), 67 (78), 82 (53), 41 (42), 55 (8), 54 (5), 68 (5), 87 (4), 81 (4), 83 (3)
50, ( <i>Z</i> )-3-hexenyl butenoate <sup>a</sup>	1403	1527	168	67 (100), 69 (80), 82 (70), 41 (53), 55 (20), 68 (12), 83 (12), 54 (10), 87 (5), 81 (4)
52, a ( <i>Z</i> )-3-hexenyl pentenoate	1528	1652	182	67 (100), 83 (89), 55 (84), 82 (84), 41 (18), 54 (10), 101 (9), 53 (8), 81 (6), 68 (3)
49, phenethyl butenoate <sup>a</sup>	1803	2050	190	104 (100), 69 (67), 41 (28), 43 (17), 51 (13), 91 (12), 78 (12), 77 (10), 55 (9), 65 (7)
56, butyl 3-hydroxybutanoate	1500	1678	160	87 (100), 43 (70), 45 (60), 56 (59), 57 (50), 89 (30), 60 (25), 69 (20), 61 (18), 85 (17)
57, isobutyl 3-hydroxybutanoate	1447	1617	160	43 (100), 87 (90), 57 (66), 45 (44), 56 (43), 41 (31), 60 (19), 89 (18), 85 (14), 69 (11)
58, isoamyl 3-hydroxybutanoate	1554	1725	174	87 (100), 43 (87), 70 (81), 71 (67), 55 (48), 45 (39), 41 (39), 67 (34), 93 (22), 79 (20)
59, ( <i>Z</i> )-3-hexenyl 3-hydroxybutanoate	1731	1914	186	67 (100), 43 (62), 82 (51), 55 (44), 45 (42), 41 (37), 87 (27), 83 (20), 69 (15), 54 (9)

<sup>a</sup> Concerning the position and configuration of the double bond, see Results and Discussion.

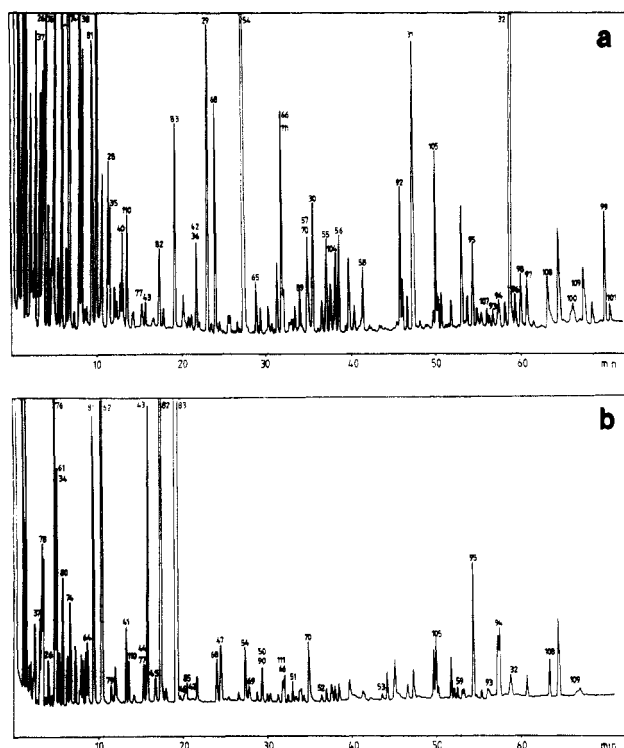


Figure 2. Gas chromatograms of the LSC fractions containing oxygenated components: (a) Baladi mango; (b) Alphonso mango (column A; peak numbers correspond to the component numbers in Table I).

by Hunter et al. (1974), we could identify esters of 3-hydroxybutanoic and 3-hydroxyhexanoic acid for the first time. Ethyl 3-hydroxybutanoate and ethyl 3-hydroxyhexanoate are known already as constituents of other tropical fruits like pineapple (Creveling et al., 1968), passion fruit (Winter and Klöti, 1972), and wood apple (MacLeod and Pieris, 1981). In this study butyl 3-hydroxybutanoate, isobutyl 3-hydroxybutanoate, and isoamyl 3-hydroxybutanoate in Baladi mango and (*Z*)-3-hexenyl 3-hydroxybutanoate in Alphonso mango were, as far as the authors know, identified for the first time as food

volatiles. Their gas chromatographic and mass spectral data are given in Table II. Butyl, isobutyl, and isoamyl 3-hydroxybutanoate possessed woody, resinous, and sherry-like notes, whereas (*Z*)-3-hexenyl 3-hydroxybutanoate had a green, fruity odor.

A further decisive difference between the two kinds of mango investigated in this study is their content of lipid oxidation products. Alphonso mango contained large amounts of  $C_6$ -aldehydes [hexanal, (*E*)-2-hexenal] and  $C_6$ -alcohols [1-hexanol, (*Z*)-3-, (*E*)-3-, and (*E*)-2-hexenol]. These components were not contained or were only detected as traces in Baladi mango, in which the amounts of unsaturated  $C_9$ -aldehydes, (*E*)-2-nonenal and (*E,Z*)-2,6-nonadienal, which belong to another group of lipid degradation products, were increased.

4-Methoxy-2,5-dimethyl-3(2*H*)-furanone, previously described in canned mango by Hunter et al. (1974), was contained in both varieties. The corresponding hydroxy compound, 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone, which was identified as a mango constituent by Pickenhagen et al. (1981), was not detected within this study. This is due to the chosen method of steam distillation to prepare the aroma extract. Initial results of a further study to investigate the more polar mango flavor components revealed 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone as well as its methyl ether to be present in ether extracts of the two mango varieties. No single identified component is characteristic of mango flavor. But the large qualitative and quantitative differences in the composition of aroma components in both varieties may partly explain their different sensory properties. Alphonso mango possessed a fresh, green, fruity note. Especially, the spectrum of (*Z*)-3-hexenyl esters, identified only in this variety, might contribute to this aroma quality. In contrast to that, Baladi mango possessed a mild, caramel-like, woody note and strongly reminded one of melon. Possibly the 3-hydroxy esters, typical for this variety, might impart this woody, resin-like note. The melon-like flavor of Baladi mangos should be related to the  $C_9$ -lipid oxidation products. In this study only (*E*)-2-nonenal and (*E,Z*)-2,6-nonadienal, known as contributing to the aroma of cucumbers (Forss et al., 1962), were detected. But the presence of

some other C<sub>9</sub> components, e.g., (*Z*)-6-nonenal or (*Z*)-6-nonenyl acetate, which were described by Buttery et al. (1982) to possess strong melon-like aroma far below the level of detection used in this study, seems probable.

**Registry No.** 1, 629-59-4; 2, 544-76-3; 3, 593-45-3; 4, 112-95-8; 5, 71-43-2; 6, 108-88-3; 7, 80-56-8; 8, 127-91-3; 9, 123-35-3; 10, 138-86-3; 11, 3338-55-4; 12, 3779-61-1; 13, 586-62-9; 14, 3856-25-5; 15, 489-40-7; 16, 87-44-5; 17, 6753-98-6; 18, 23986-74-5; 19, 24703-35-3; 20, 473-13-2; 21, 39029-41-9; 22, 483-76-1; 23, 623-42-7; 24, 141-78-6; 25, 97-62-1; 26, 105-54-4; 27, 108-64-5; 28, 123-66-0; 29, 106-32-1; 30, 110-38-3; 31, 106-33-2; 32, 124-06-1; 33, 628-97-7; 34, 123-86-4; 35, 109-21-7; 36, 626-82-4; 37, 110-19-0; 38, 539-90-2; 39, 123-92-2; 40, 106-27-4; 41, 142-92-7; 42, 2639-63-6; 43, 3681-71-8; 44, 3681-82-1; 45, 2497-18-9; 46, 33467-74-2; 47, 16491-36-4; 48, 103-45-7; 49, 85762-16-9; 50, 85762-17-0; 51, 65405-80-3; 52, 85762-18-1; 53, 53398-87-1; 54, 5405-41-4; 55, 2305-25-1; 56, 53605-94-0; 57, 85762-19-2; 58, 85762-20-5; 59, 85762-21-6; 60, 96-22-0; 61, 66-25-1; 62, 6728-26-3; 63, 1335-39-3; 64, 110-43-0; 65, 18829-56-6; 66, 557-48-2; 67, 593-08-8; 68, 98-01-1; 69, 100-52-7; 70, 122-78-1; 71, 432-25-7; 72, 23726-93-4; 73, 79-77-6; 74, 71-36-3; 75, 78-92-2; 76, 78-83-1; 77, 556-82-1; 78, 115-18-4; 79, 71-41-0; 80, 6032-29-7; 81, 123-51-3; 82, 111-27-3; 83, 928-96-1; 84, 928-97-2; 85, 928-95-0; 86, 36653-82-4; 87, 60-12-8; 88, 98-55-5; 89, 138-87-4; 90, 78-70-6; 91, 1197-06-4; 92, 1197-07-5; 93, 19888-33-6; 94, 19888-34-7; 95, 1139-30-6; 96, 489-41-8; 97, 552-02-3; 98, 21284-22-0; 99, 481-34-5; 100, 50895-55-1; 101, 16641-47-7; 102, 96-48-0; 103, 108-29-2; 104, 695-06-7; 105, 104-50-7; 106, 698-76-0; 107, 82373-92-0; 108, 706-14-9; 109, 705-86-2; 110, 513-86-0; 111, 4077-47-8; 112, 2628-17-3; 113, 71750-42-0; 114, 95-16-9.

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## Deterioration Mechanism of Lemon Flavor. 2. Formation Mechanism of Off-Odor Substances Arising from Citral

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*p*-Mentha-1,5-dien-8-ol (**3a**) and *p*-mentha-1(7),2-dien-8-ol (**3b**) were isolated from deteriorated citral as major components and were identified by IR, EI-MS, FI-MS, <sup>1</sup>H NMR, and <sup>13</sup>C NMR. When **3a** or **3b** was treated with aqueous citric acid, an equilibrium mixture of **3a-3b** isomers (55:45) resulted and both isomers were subsequently converted to *p*-cymen-8-ol (**6**) by disproportionation and redox reactions. Further, the more stable *p*-cymene (**9**) and  $\alpha$ ,*p*-dimethylstyrene (**8**), which are responsible for the off-odor of deteriorated lemon, were formed from **3** and **6**. This deterioration mechanism was also confirmed by mass chromatography studies. The existence of *p*-menth-1-ene-3,8-diol (extremely unstable in acidic conditions) was suggested by isolation of 3-ethoxy-*p*-menth-1-en-8-ol (**4**).

So far, studies on the fate of citral under acidic conditions have been carried out in connection with the deterioration flavor of alcoholic lemon beverages or concentrated lemon juice (Iwata et al., 1968; Iwata and Yamamoto, 1978; Kimura and Iwata, 1978a,b; Kimura et al., 1981, 1982). Citral, one of the significant components of lemon oil (Ikeda et al., 1962; Lund and Bryan, 1976), was rapidly cyclized to give *p*-cymene (**9**) and  $\alpha$ ,*p*-dimethylstyrene (**8**) in Scheme I, which are responsible for lemon off-odor (Iwata and Yamamoto, 1978).

Compound **8** has been isolated and identified as an acid-catalyzed cyclization product of citral and in the

distilled essential lime oil (Loori and Cover, 1964; Slater and Watkins, 1964).

These have been several recent publications on the cyclization of citral (Baines et al., 1970; Clark et al., 1977; McHale et al., 1979). However, unequivocal evidence to confirm the deterioration mechanism still appears to be lacking, since pure compounds (**3a** and **3b**) were not used to precisely elucidate the individual pathway. We deal here with the detailed identification of intermediates of off-odor substances arising from citral and with the further fate of such intermediates in an aqueous citric acid solution.

#### EXPERIMENTAL SECTION

**Instrumentation.** Analyses by gas-liquid chromatography (GLC) were performed on a JEOL JGC-20KFP equipped with glass capillary SCOT column (30 m  $\times$  0.28 mm i.d.), coated with DEGS. The oven temperature was programmed from 50 to 160  $^{\circ}$ C at 3  $^{\circ}$ C/min. The injector

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