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## Volatile Constituents from Guava (*Psidium guajava*, L.) Fruit

Heinz Idstein and Peter Schreier\*

Concentrates of fresh guava (*Psidium guajava*, L.) fruit pulp were obtained by standard controlled high-vacuum distillation with subsequent solvent extraction (pentane-dichloromethane, 2:1) and silica gel LC pre separation using a pentane-diethyl ether gradient. The concentrates were analyzed by capillary gas chromatography and coupled capillary gas chromatography techniques, i.e., on-line mass spectrometry and FTIR spectroscopy. A total of 154 substances was identified, from which 116 compounds could be described for the first time as guava fruit constituents. Quantitatively, lipid peroxidation products such as C<sub>6</sub> aldehydes and alcohols were predominant.

Guava is the fruit of *Psidium guajava*, L., a tree native to the American tropics. The round-oval fruit is green-yellow and shows a light yellow or pink pulp. The aroma impression of the fruit is often described as "quince banana" like (Herrmann, 1983).

Several publications about guava fruit volatiles have already been provided; the literature until 1978 has been reviewed by Shiota (1978). Recent studies were carried out by McLeod and Gonzales de Troconis (1982) and Shiota et al. (1980), the latter comparing the volatiles of strawberry guava (*Psidium cattelium*, Sabine), yellow guava (*Psidium cattelium* Sabine var. *lucidum* Hort.), and feijoa (*Feijoa sellowiana* Berg). Additional work has also been done exclusively on the volatile constituents of feijoa (Hardy and Michael, 1970; Shaw et al., 1983).

### EXPERIMENTAL SECTION

**Fruits.** Fresh ripe guava fruits (*P. guajava*, L.) were transported by air freight from Brazil and were analyzed the day after arrival.

**Sample Preparation.** A total of 3.3 kg of fruit pulp was obtained from 3.9 kg of total fruit after removal of the skin, homogenization by a Waring blender, and separation by a hydraulic press (Hafico). After addition of internal

standards (butylbenzene, 0.98 mg; dimethyl fumarate, 1.27 mg; 1-decanol, 1.0 mg), the pulp was subjected to high-vacuum distillation.

**High-Vacuum Distillation.** In a 4-L three-neck flask an aliquot (1.1 kg) of the pulp was diluted with water (1 L) and high-vacuum distilled (40-50 °C/0.1 bar). Approximately 1 L of distillate was collected in two dry ice-methanol (-25 °C) and in two liquid nitrogen cooled traps. The four traps were thawed and the contents were combined for the following solvent extraction. In total, 3.3 kg of fruit pulp was distilled in three batches. The distillation residues were set aside for subsequent analysis of non-distillable aroma compounds by direct solvent extraction.

**Liquid-Liquid Extraction.** The aqueous distillates and the distillation residues were each extracted with pentane-dichloromethane (2:1) in several portions over 24 h (Drawert and Rapp, 1968). Each of the two extracts were dried over anhydrous sodium sulfate and carefully concentrated to approximately 0.2 mL by using a Vigreux column (45 °C).

**Column Chromatography on Silica Gel.** The concentrated extracts obtained from distillates were fractionated on silica gel 60 (Merck), activity grade II, by using a pentane-diethyl ether gradient (Idstein et al., 1984). Cooled (11-13 °C) glass columns, 2.0 cm i.d. × 30 cm, were used. The elution rate was 60 mL/h; three fractions were separated. Fraction I was eluted with 250 mL of pentane, fraction II was obtained by eluting with 250 mL of diethyl

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ether-pentane (1:9 v/v), and fraction III was obtained by eluting with 250 mL of diethyl ether. All eluates were dried over anhydrous sodium sulfate and concentrated to 0.2 mL (for HRGC and HRGC-MS study) and to 0.05 mL (for HRGC-FTIR analysis), respectively.

**Capillary Gas Chromatography (HRGC).** A Carlo Erba Fractovap 4160 gas chromatograph with FID equipped with a J & W fused silica wide-bore CW 20 M capillary column (30 m, 0.31-mm i.d., film thickness = 0.15  $\mu$ m) with a 2-m uncoated fused silica capillary precolumn as the "retention gap" (Grob and Müller, 1982) was used. On-column injection with an air-cooled injection system was employed. The temperature program was 50–240 °C at 2 °C/min. The flow rates for the carrier gas were 2.5 mL/min He, for the make-up gas 30 mL/min N<sub>2</sub>, and for the detector gases 30 mL/min H<sub>2</sub> and 300 mL/min air, respectively. The detector temperature was kept at 220 °C. Volumes of 0.3  $\mu$ L were injected.

Results of qualitative analyses were verified by comparison of HRGC retention, mass spectral, and, in part, FTIR vapor-phase data with those of authentic reference substances. Quantitative HRGC determinations were carried out by standard controlled calculations using a Hewlett-Packard 3388 A laboratory data system without consideration of distillation and extraction yields (calibration factors for all compounds,  $F = 1.00$ ).

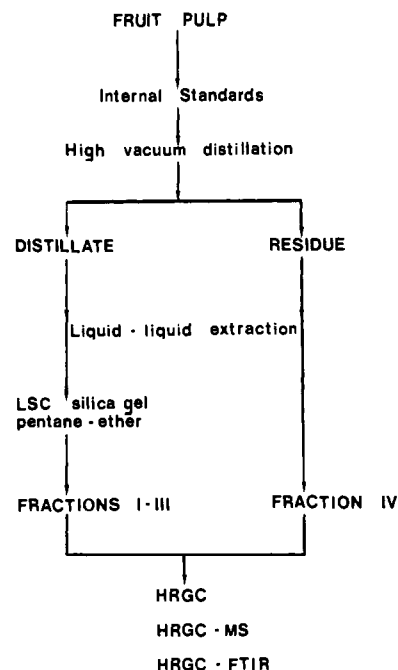
**Capillary Gas Chromatography-FTIR Spectroscopy (HRGC-FTIR).** A Bruker IFS 85 FTIR system with an HRGC interface and a 36  $\times$  1.5 mm light pipe (Bruker), maintained at 200 °C, and a liquid nitrogen cooled Hg-Cd-Te detector (600–4800 cm<sup>-1</sup>) was used. A spectral resolution of 8 cm<sup>-1</sup> at a scan rate of 12 spectra/s was chosen. As the gas chromatograph a Carlo Erba Fractovap 4160 apparatus was employed equipped with a 30 m  $\times$  0.32 mm Chrompack CP 57 CB fused silica capillary WSCOT column (df = 1.2  $\mu$ m), connected to a 2-m uncoated piece of fused silica capillary as the "retention gap" (Grob and Müller, 1982). The carrier gas flow rate was 2.3 mL/min He. On-column injection with an air-cooled system was used. The temperature program was 50–130 °C at 2 °C/min and 130–200 °C at 5 °C/min. Injection volumes were 0.5  $\mu$ L.

**Capillary Gas Chromatography-Mass Spectrometry.** A Varian Aerograph 1440 gas chromatograph equipped with a Carlo Erba water-cooled on-column injection system was coupled by an open-split interface to a Finnigan MAT 44 mass spectrometer. A MEGA CW 20 M fused silica capillary column (25 m, 0.32-mm i.d., film thickness = 1.0  $\mu$ m) connected to a 2-m uncoated piece of fused silica capillary column as the "retention gap" (Grob and Müller, 1982) was used. The conditions were as follows: temperature, isothermal for 5 min at 60 °C and then from 60 to 240 °C at 2 °C/min; carrier gas flow rate, 2.5 mL/min He; temperature of ion source and all connection parts, 200 °C; electron energy, 70 eV; cathodic current, 0.8 mA; injection volumes, 0.3  $\mu$ L.

## RESULTS AND DISCUSSION

In Figure 1 the analytical steps of our study on guava fruit volatiles are schematically outlined. The aroma concentrates obtained were investigated by capillary gas chromatography (HRGC) and capillary gas chromatography-mass spectrometry (HRGC-MS). For the study of silica gel fraction II, additionally, capillary gas chromatography-FTIR spectroscopy was used (Schreier et al., 1984).

The results of HRGC separation of guava volatiles in the concentrates obtained by high-vacuum distillation-solvent extraction and subsequent silica gel fractionation



**Figure 1.** Analytical steps of sample preparation, separation, and identification of guava fruit pulp volatiles.

**Table I.** Volatile Compounds Identified in Guava Fruit Pulp by HRGC and HRGC-MS (Silica Gel Fraction I)

peak no. <sup>a</sup>	compound	mass spectral data <sup>b</sup>
<b>Hydrocarbons</b>		
1	methylcyclohexane <sup>c</sup>	83, 55, 41, 98
2	octane	43, 41, 57, 71
4	nonane <sup>c</sup>	43, 41, 57, 71
9	decane <sup>c</sup>	43, 41, 57, 71
10	toluene	91, 92, 65, 51
16	undecane <sup>c</sup>	43, 41, 57, 71
16	ethylbenzene <sup>c</sup>	91, 106, 51, 65
17	<i>p</i> -xylene <sup>c</sup>	91, 106, 105, 77
18	$\beta$ -myrcene	41, 93, 69, 91
20	limonene	68, 67, 93, 41
21	propylbenzene <sup>c</sup>	91, 120, 65, 51
24	dodecane <sup>c</sup>	57, 43, 71, 41
26	( <i>Z</i> )-ocimene	93, 41, 79, 91
27	vinylbenzene <sup>c</sup>	104, 78, 51, 103
29	<i>p</i> -cymene <sup>c</sup>	119, 91, 134, 117
30	1-methyl-2-ethylbenzene <sup>c</sup>	105, 120, 91, 77
31	terpinolene <sup>c</sup>	93, 121, 136, 91
32	butylbenzene (int. std)	91, 92, 134, 65
33	tridecane <sup>c</sup>	57, 43, 71, 85
40	tetradecane <sup>c</sup>	57, 71, 43, 85
41	2,5-dimethylstyrene <sup>c</sup>	117, 132, 115, 91
45	pentadecane <sup>c</sup>	57, 43, 71, 85
47	hexadecane <sup>c</sup>	57, 43, 71, 85
<b>S-Containing Volatiles</b>		
6	3-pentanethiol <sup>c</sup>	43, 61, 55, 41
12	dimethyl disulfide <sup>c</sup>	94, 45, 79, 45
13	2-methylthiophene <sup>c</sup>	97, 98, 53, 99
14	3-methylthiophene <sup>c</sup>	97, 98, 45, 59
19	2-ethylthiophene <sup>c</sup>	97, 112, 45, 54
35	dimethyl trisulfide <sup>c</sup>	45, 79, 47, 126
<b>Miscellaneous</b>		
23	2-pentylfuran <sup>c</sup>	81, 82, 138, 53

<sup>a</sup>The peak numbers correspond to the numbers in Figure 2.

<sup>b</sup>The four most intensive peaks are represented (M<sup>+</sup> in italics).

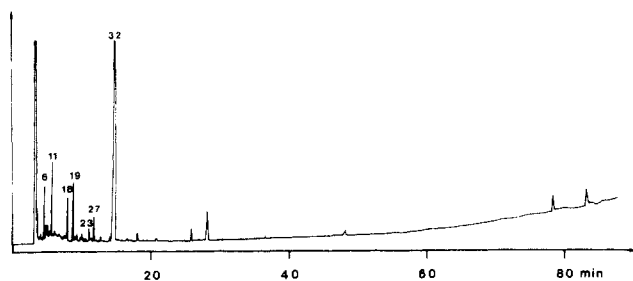
<sup>c</sup>Reported for the first time as a guava fruit constituent.

are outlined in Figures 2–4. The compounds identified by HRGC and HRGC-MS in these fractions as well as in the concentrates obtained by liquid-liquid extraction of the distillation residues are represented in Tables I–III. In total, 41 carbonyls, 35 esters, 25 alcohols, 22 hydro-

**Table II. Volatile Compounds Identified in Guava Fruit Pulp by HRGC, HRGC-MS, and HRGC-FTIR (Silica Gel Fraction II)**

peak no. <sup>a</sup>	compound	mass spectral data <sup>b</sup>	peak no. <sup>a</sup>	compound	mass spectral data <sup>b</sup>
<b>Esters</b>			<b>Carbonyls</b>		
1	ethyl acetate	43, 45, 61, 70	7	3-pentanone	57, 86, 58, 56
5	ethyl propanoate <sup>c</sup>	57, 45, 74, 75	8	pentanal	44, 41, 58, 43
6	propyl acetate <sup>c</sup>	43, 61, 73, 42	9	1-penten-3-one <sup>c</sup>	55, 84, 56, 57
10	ethyl butanoate	43, 71, 88, 41	11	hexanal <sup>d</sup>	44, 41, 43, 56
16	ethyl pentanoate <sup>c</sup>	88, 85, 57, 60	12	(Z)-2-pentenal <sup>c</sup>	55, 41, 83, 84
18	ethyl (E)-2-butenolate <sup>c</sup>	69, 41, 99, 68	13	(E)-2-pentenal <sup>c,d</sup>	55, 41, 83, 84
21	methyl hexanoate	74, 87, 59, 55	14	(Z)-3-hexenal <sup>c,d</sup>	41, 69, 55, 42
26	ethyl hexanoate <sup>d</sup>	43, 88, 60, 99	17	4-methylheptan-3-one <sup>c</sup>	43, 57, 71, 41
29	3-methylbutyl butanoate <sup>c</sup>	43, 71, 70, 55	22	heptanal <sup>c</sup>	44, 43, 42, 41
30	methyl (Z)-3-hexenoate <sup>c</sup>	41, 68, 74, 69	24	(E)-3-hexenal <sup>c</sup>	41, 55, 83, 69
33	hexyl acetate <sup>d</sup>	43, 56, 41, 55	25	(E)-2-hexenal <sup>d</sup>	41, 55, 69, 42
35	(E)-2-hexenyl acetate <sup>c</sup>	43, 67, 41, 82	27	3-octanone <sup>e</sup>	43, 57, 72, 99
36	(Z)-3-hexenyl acetate <sup>d</sup>	67, 41, 82, 55	34	1-octen-3-one <sup>c</sup>	70, 55, 43, 97
38	ethyl (E)-2-hexenoate <sup>c</sup>	55, 97, 41, 99	37	6-methyl-5-hepten-2-one	43, 41, 55, 69
41	(Z)-3-hexenyl methylpropanoate <sup>c</sup>	43, 67, 82, 41	42	(E,E)-2,4-hexadienal <sup>c</sup>	81, 41, 53, 96
44	methyl octanoate <sup>c</sup>	74, 43, 87, 41	45	1-methyl-3-cyclohexen-1-carboxaldehyde <sup>c</sup>	95, 109, 41, 81
48	ethyl octanoate	88, 43, 57, 41	46	(E)-2-octenal <sup>c,d</sup>	44, 41, 55, 42
57	dimethyl fumarate (int. std)	113, 85, 59, 53	49	(E,Z)-2,4-heptadienal <sup>c,d</sup>	81, 41, 53, 110
61	methyl 2-furoate <sup>c</sup>	95, 126, 68, 96	51	(E,E)-2,4-heptadienal <sup>c</sup>	81, 41, 53, 110
66	methyl benzoate	105, 77, 51, 136	52	decanal <sup>c</sup>	41, 43, 57, 44
67	2-cyclohexyl acetate <sup>c</sup>	82, 81, 67, 43	54	benzaldehyde	77, 105, 106, 51
68	ethyl 2-furoate <sup>c</sup>	95, 112, 96, 140	62	(E,E)-2,4-octadienal <sup>c</sup>	81, 41, 67, 124
73	(Z)-3-hexenyl hexanoate	67, 82, 43, 41	63	(E,Z)-2,6-nonadienal <sup>c</sup>	41, 70, 69, 67
75	(Z)-2-hexenyl hexanoate <sup>c</sup>	43, 41, 99, 67	72	acetophenone <sup>c</sup>	77, 105, 51, 120
76	ethyl benzoate <sup>d,e</sup>	105, 77, 51, 122	74	(E)-2-decenal <sup>c</sup>	44, 41, 43, 42
78	(E)-2-hexenyl hexanoate <sup>c</sup>	43, 99, 55, 41	81	(E,E)-2,4-nonadienal <sup>c</sup>	81, 41, 67, 138
80	(E)-3-hexenyl hexanoate <sup>c</sup>	67, 82, 43, 41	84	carvone <sup>c</sup>	82, 54, 108, 93
92	ethyl phenylacetate <sup>c</sup>	91, 164, 92, 65	91	(Z,E)-2,4-decadienal <sup>c</sup>	81, 41, 83, 152
109	3-phenylpropyl acetate <sup>d</sup>	117, 118, 43, 91	96	(E,E)-2,4-decadienal <sup>d</sup>	81, 41, 83, 152
110	methyl (Z)-cinnamate <sup>c</sup>	131, 103, 77, 162	115	3-phenyl-2-propenal <sup>c</sup>	131, 51, 77, 103
117	methyl (E)-cinnamate	131, 103, 77, 162			
121	ethyl (E)-cinnamate <sup>e</sup>	131, 77, 51, 103			
122	cinnamyl acetate	43, 115, 116, 117			
128	methyl hexadecanoate <sup>c</sup>	74, 87, 43, 55			
			<b>Miscellaneous</b>		
			53	(Z)-theaspirane <sup>c</sup>	138, 82, 96, 41
			56	(E)-theaspirane <sup>c</sup>	138, 82, 96, 41
			59	1-phenoxybutane <sup>c</sup>	84, 150, 41, 77
			69	acetylpyrazine <sup>c</sup>	43, 122, 80, 79
			87	1,2-dimethoxybenzene <sup>c</sup>	138, 77, 95, 123
			111	(E)-2-hexenoic acid <sup>c</sup>	73, 42, 41, 55
			131	2-methylthiobenzothiazole <sup>c,f</sup>	181, 148, 135, 108

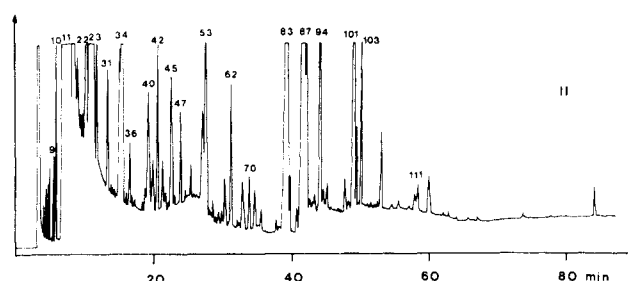
<sup>a</sup>The peak numbers correspond to the numbers in Figure 3. <sup>b</sup>The four most intensive peaks are represented (M<sup>+</sup> in italics). <sup>c</sup>Reported for the first time as a guava fruit constituent. <sup>d</sup>Additionally identified by HRGC-FTIR analysis. <sup>e</sup>Already described as a constituent in *Feijoa sellowiana*, L. <sup>f</sup>Only detectable in the distillation residue.



**Figure 2.** HRGC separation of guava fruit pulp volatiles (silica gel fraction I) after on-column injection on a J & W 30 m × 0.31 mm fused silica WCOT capillary CW 20 M, df = 0.15 μm. The peak numbers correspond to the numbers in Table I.

carbons, 13 acids, 9 S-containing compounds, and 9 substances with miscellaneous structures could be identified, from which 15 were only detectable in the distillation residues. A total of 116 compounds were described for the first time as guava fruit constituents.

The quantitative distribution of the major guava volatiles is outlined in Table IV. A total amount of 69 mg/kg of pulp was determined, from which the major part (51 mg/kg) was detected in the mid-polarity silica gel fraction II. In this fraction the substances occurring in the highest concentrations were found, i.e., (E)-2-hexenal (25 mg/kg), hexanal (4 mg/kg), and (Z)-3-hexenyl acetate (2 mg/kg),



**Figure 3.** HRGC separation of guava fruit pulp volatiles (silica gel fraction II) after on-column injection on a J & W 30 m × 0.31 mm fused silica WCOT capillary CW 20 M, df = 0.15 μm. The peak numbers correspond to the numbers in Table II.

respectively. In the polar fraction III, an amount of 18 mg/kg was established with (Z)-3-hexen-1-ol (6 mg/kg) and 1-hexanol (2 mg/kg) as major constituents. In the nonpolar fraction I only a content of 0.2 mg/kg was found; all volatile constituents in this fraction were determined in concentrations <50 μg/kg.

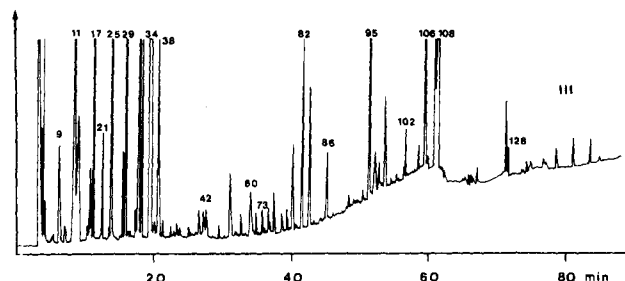
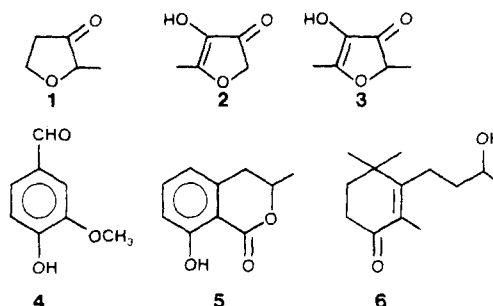
Qualitatively and quantitatively, the carbonyls occupy a special place among the guava fruit volatiles. Fifty percent of the total amount consists of aldehydes. Most of them are typical products of peroxidation of unsaturated fatty acids (Frankel, 1982; Grosch, 1982). Among the keto compounds, some volatiles have to be considered as lipid

**Table III. Volatile Compounds Identified in Guava Fruit Pulp by HRGC and HRGC-MS (Silica Gel Fraction III)**

peak no. <sup>a</sup>	compound	mass spectral data <sup>b</sup>
<b>Alcohols</b>		
5	2-butanol <sup>c</sup>	45, 59, 41, 44
13	2-pentanol <sup>c</sup>	45, 44, 43, 55
15	1-butanol <sup>c</sup>	56, 41, 43, 42
16	1-penten-3-ol	57, 67, 68, 58
21	1-pentanol	42, 41, 44, 68
28	( <i>E</i> )-2-pentanol <sup>c</sup>	57, 41, 44, 43
29	( <i>Z</i> )-2-pentanol <sup>c</sup>	57, 41, 44, 43
32	1-hexanol	56, 43, 41, 55
33	( <i>E</i> )-3-hexanol <sup>c</sup>	41, 67, 55, 69
34	( <i>Z</i> )-3-hexanol	41, 67, 55, 42
38	( <i>E</i> )-2-hexanol <sup>c</sup>	57, 41, 67, 82
40	1-octen-3-ol <sup>c</sup>	57, 43, 41, 72
42	1-heptanol <sup>c</sup>	56, 43, 70, 41
53	1-octanol	56, 41, 55, 43
61	4-terpinenol	71, 43, 41, 93
62	3-decanol <sup>c</sup>	59, 69, 55, 41
64	( <i>E</i> )-2-octen-1-ol <sup>c</sup>	41, 54, 67, 57
68	5-undecanol <sup>c</sup>	55, 83, 101, 41
82	1-decanol (int. std.)	53, 41, 55, 56
89	2-phenylethanol	91, 92, 65, 122
101	3-phenylpropanol	116, 117, 91, 92
108	eugenol <sup>c</sup>	55, 77, 164, 51
115	1-tetradecanol <sup>c</sup>	43, 41, 55, 57
119	cinnamyl alcohol <sup>d</sup>	92, 77, 78, 91
128	1-hexadecanol <sup>c</sup>	43, 55, 57, 41
143	1-octadecanol <sup>c</sup>	43, 55, 57, 41
<b>Carbonyls</b>		
6	1-penten-3-one <sup>c</sup>	55, 84, 56, 57
7	( <i>E</i> )-2-butenal <sup>c</sup>	41, 70, 69, 44
15	2-methyl-4-pentenal <sup>c</sup>	41, 69, 55, 83
23	2-methyltetrahydrofuran-3-one <sup>c</sup>	43, 72, 100, 45
25	3-hydroxy-2-butanone <sup>c</sup>	45, 43, 42, 88
60	5,6-dihydro-2 <i>H</i> -pyran-2-carboxaldehyde <sup>c</sup>	83, 55, 57, 112
95	4-hydroxy-5-methyl-3(2 <i>H</i> )-furanone <sup>c</sup>	57, 85, 43, 67
99	2,5-dimethyl-4-hydroxy-3(2 <i>H</i> )-furanone <sup>c,d</sup>	43, 57, 128, 85
136	3,4-dihydro-8-hydroxy-3-methyl-2-benzot-1 <i>H</i> -pyran-1-one <sup>c,d</sup>	134, 178, 78, 51
141	vanillin <sup>c</sup>	152, 151, 81, 109
150	4-oxo-dihydro- $\beta$ -ionol <sup>c,d</sup>	43, 41, 67, 109
<b>Esters</b>		
67	methyl 4-hydroxybutanoate <sup>c,d</sup>	43, 74, 61, 73
80	methyl nicotinoate <sup>c</sup>	78, 106, 51, 137
<b>Acids</b>		
39	acetic acid <sup>c</sup>	43, 45, 60, 42
65	butanoic acid <sup>c</sup>	60, 73, 42, 43
86	hexanoic acid	60, 73, 41, 43
94	heptanoic acid <sup>c</sup>	60, 43, 41, 87
102	octanoic acid <sup>c</sup>	60, 73, 43, 55
110	nonanoic acid <sup>c,d</sup>	60, 73, 57, 55
122	decanoic acid <sup>c,d</sup>	60, 72, 41, 43
131	benzoic acid <sup>c,d</sup>	105, 122, 77, 51
146	phenylpropanoic acid <sup>c,d</sup>	91, 104, 150, 77
148	tetradecanoic acid <sup>c,d</sup>	73, 60, 43, 41
152	cinnamic acid <sup>c,d</sup>	147, 148, 103, 51
155	hexadecanoic acid <sup>c,d</sup>	43, 73, 60, 57
<b>Miscellaneous</b>		
22	methylpyrazine <sup>c</sup>	94, 67, 53, 42
36	2,3,5-trimethylpyrazine <sup>c</sup>	42, 122, 81, 54
73	5-ethoxythiazole <sup>c</sup>	45, 101, 46, 129
92	benzothiazole	135, 108, 69, 63
106	$\gamma$ -decalactone <sup>c</sup>	85, 41, 43, 55

<sup>a</sup>The peak numbers correspond to the numbers in Figure 4.<sup>b</sup>The four most intensive peaks are represented (M<sup>+</sup> in italics).<sup>c</sup>Reported for the first time as a guava fruit constituent. <sup>d</sup>Only detectable in the distillation residue.

degradation products, too, e.g., 1-penten-3-one and 1-octen-3-one (Grosch, 1982), whereas the main constituent in this class, 3-hydroxy-2-butanone, may originate from a side

**Figure 4.** HRGC separation of guava fruit pulp volatiles (silica gel fraction III) after on-column injection on a J & W 30 m  $\times$  0.31 mm fused silica WCOT capillary CW 20 M, df = 0.15  $\mu$ m. The peak numbers correspond to the numbers in Table III.**Figure 5.** Selected oxo compounds newly identified as guava fruit pulp volatiles: 1, 2-methyltetrahydrofuran-3-one; 2, 4-hydroxy-5-methyl-3(2*H*)-furanone; 3, 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone; 4 vanillin; 5, 3,4-dihydro-8-hydroxy-3-methyl-2(1*H*)-benzopyran-1-one; 6, 4-oxodihydro- $\beta$ -ionol.

reaction of the biogenesis of valine and leucine (Piendl, 1969).

Another qualitatively important class of volatiles consists of esters. In this group, C<sub>2</sub> residues with a series of ethyl esters and acetates predominate, biogenetically derived from  $\beta$ -oxidation of corresponding fatty acids (Tressl et al., 1975). Esters with unsaturated C<sub>6</sub> residues could also originate from side reactions of  $\beta$ -oxidation of fatty acids (Engel and Tressl, 1983), but due to the presence of high amounts of C<sub>6</sub> aldehydes and alcohols, a biogenetic pathway involving enzymic oxidation and reduction steps of C<sub>6</sub> compounds should also be considered.

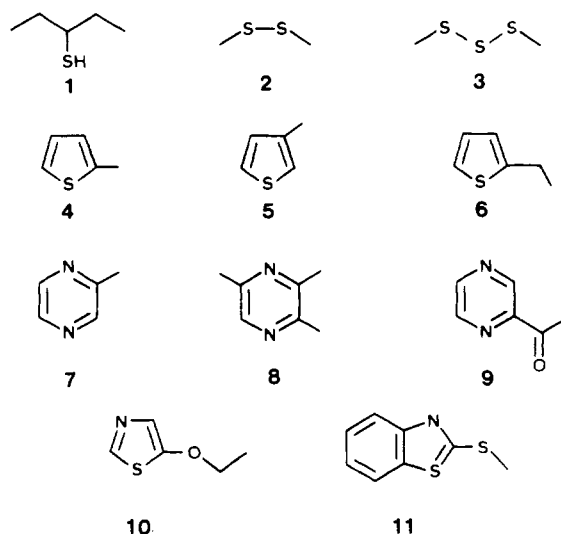
Among the esters some "exotic" methyl derivatives are remarkable, e.g., methyl nicotinoate, a compound that is not very common among fruit volatiles (Pyysalo, et al., 1979; McLeod and Pieris, 1981), or the *Z* isomer of methyl cinnamate, previously only detected in rhubarb (Frattini et al., 1974), Turkey mullein (Schultz et al., 1980), and matsutake (Yajima et al., 1981), respectively. In additional investigations the *Z*-configured free acid could be also detected among the guava fruit constituents (Idstein et al., 1985). Together with the identified benzoates, phenyl acetates, and phenylpropyl and cinnamoyl esters, the latter compound belongs to the large group of phenylpropane derivatives. The occurrence of these substances in guava fruit shows the chemotaxonomic relation within various plants of the *Myrtaceae* family, e.g., muscat (*Myristica fragrans*), pimento (*Pimenta odorata*), or clove (*Syzygium aromaticum*), where in the essential oils phenylpropane derivatives are comprising the major volatiles (Masada, 1976).

The aliphatic alcohols detected in guava fruit pulp originate from fatty acid metabolism. The unsaturated compounds and the short-chain saturated alcohols are related to lipid peroxidation, whereas the long-chain alcohols >C<sub>14</sub> can be regarded as enzymic reaction products of  $\alpha$ -oxidation of corresponding fatty acids (Galliard and Matthew, 1976). Phenylpropanol, cinnamic alcohol, and

Table IV. Quantitative Distribution of Main Constituents of Guava Fruit Volatiles

10–50 µg/kg of pulp <sup>a</sup>	50–250 µg/kg of pulp <sup>a</sup>	250–1250 µg/kg of pulp <sup>a</sup>	>1250 µg/kg of pulp <sup>a</sup>
3-pentanone	4-methylheptan-3-one	3-hydroxy-2-butanone	hexanal
1-penten-3-one	6-methyl-5-hepten-2-one	(Z)-2-pentenal	(E)-2-hexenal
acetophenone	3-octanone	(E)-2-pentenal	
carvone	1-octen-3-one	(E)-2-octenal	
(E)-2-butenal	(E,E)-2,4-heptadienal	(E,Z)-2,4-heptadienal	
pentanal	(E,E)-2,4-nonadienal	(E,E)-2,4-decadienal	
heptanal	(E,Z)-2,6-nonadienal		
	decanal		
	(E)-2-decenal		
	benzaldehyde		
ethyl propanoate	ethyl phenylacetate	hexyl acetate	(Z)-3-hexenyl acetate
methyl 2-furoate	cinnamyl acetate	(E)-2-hexenyl acetate	
	ethyl butanoate	3-phenylpropyl acetate	
	3-methylbutyl butanoate	ethyl (E)-2-butenate	
	methyl hexanoate	ethyl hexanoate	
	methyl (Z)-3-hexenoate	methyl octanoate	
	ethyl (E)-2-hexenoate	methyl benzoate	
	ethyl octanoate		
	ethyl benzoate		
	methyl (Z)-cinnamate		
	methyl (E)-cinnamate		
	ethyl (E)-cinnamate		
3-pentanethiol	1-pentanol	1-penten-3-ol	1-hexanol
1-octanol		(Z)-2-penten-1-ol	(Z)-3-hexen-1-ol
1-octen-3-ol		(E)-2-hexen-1-ol	
(E)-2-octen-1-ol		(E)-3-hexen-1-ol	
5-undecanol			
2-phenylethanol			
dimethyl disulfide	(E)-theaspirane		
(Z)-theaspirane			
2,3,5-trimethylpyrazine			

<sup>a</sup>Standard controlled capillary gas chromatographic determinations in fruit pulp, without consideration of calibration factors, i.e.,  $F = 1.00$  for all compounds.



**Figure 6.** N- and S-containing volatiles newly identified as guava fruit pulp volatiles: 1, 3-pentanethiol; 2, dimethyl disulfide; 3, dimethyl trisulfide; 4, 2-methylthiophene; 5, 3-methylthiophene; 6, 2-ethylthiophene; 7, methylpyrazine; 8, 2,3,5-trimethylpyrazine; 9, acetylpyrazine; 10, 5-ethoxythiazole; 11, 2-methylthiobenzothiazole.

eugenol can be regarded as reduction products of cinnamic acids (Grisebach, 1981).

Another group of homogeneous biogenetic origin consists of so-called norcarotenoids, i.e., hypothetical biodegradation products of higher terpenes. To this group the newly identified 4-oxodihydro- $\beta$ -ionol, only detectable in the distillation residues of the pulp, belongs as an interesting compound; it can be considered as a hydroxylation product of megastigmadienones, which have been reported to be present in tobacco and yellow passion fruit (Demole et al., 1979).

A further interesting group of guava aroma substances is represented by the 3(2H)-furanones (Figure 5). Their occurrence and importance in various fruit aromas are well-known (Rodin et al., 1965; Ohloff, 1969; Pickenhagen et al., 1981). Furthermore, a certain amount of N- and S-heteroatomic compounds seems to be characteristic for the guava aroma. In Figure 6, S- and N-containing volatiles newly detected as trace compounds in guava fruit pulp are summarized. The formation of di- and trisulfides can be understood from the enzymic degradation of alkylcysteine sulfoxides (Stoll and Seebeck, 1951). Practically nothing is known about the biogenetic formation of thiophenes, pyrazines, and thiazoles in plants; commonly these substances are found as chemical reaction products in so-called reaction flavors (Waller and Feather, 1983).

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**Registry No.** Methylcyclohexane, 108-87-2; octane, 111-65-9; nonane, 111-84-2; decane, 124-18-5; toluene, 108-88-3; undecane, 1120-21-4; ethylbenzene, 100-41-4; *p*-xylene, 106-42-3;  $\beta$ -myrcene, 123-35-3; limonene, 138-86-3; propylbenzene, 103-65-1; dodecane, 112-40-3; (Z)-ocimene, 27400-71-1; vinylbenzene, 100-42-5; *p*-cymene, 99-87-6; 1-methyl-2-ethylbenzene, 611-14-3; terpinolene, 586-62-9; tridecane, 629-50-5; tetradecane, 629-59-4; 2,5-dimethylstyrene, 2039-89-6; pentadecane, 629-62-9; hexadecane, 544-76-3; 3-pentanethiol, 616-31-9; dimethyl disulfide, 624-92-0; 2-methylthiophene, 554-14-3; 3-methylthiophene, 616-44-4; 2-ethylthiophene, 872-55-9; dimethyl trisulfide, 3658-80-8; ethyl acetate, 141-78-6; ethyl propanoate, 105-37-3; propyl acetate, 109-60-4; ethyl butanoate, 105-54-4; ethyl pentanoate, 539-82-2; ethyl (E)-2-butenate, 623-70-1; methyl hexanoate, 106-70-7; ethyl hexanoate, 123-66-0; 3-methylbutyl butanoate, 106-27-4; methyl (Z)-3-hexenoate, 13894-62-7; hexyl acetate, 142-92-7; (E)-2-hexenyl acetate, 2497-18-9; (Z)-3-hexenyl acetate, 3681-71-8; ethyl (E)-

2-hexenoate, 27829-72-7; (Z)-3-hexenyl methylpropanoate, 41519-23-7; methyl octanoate, 111-11-5; ethyl octanoate, 106-32-1; methyl 2-furoate, 611-13-2; methyl benzoate, 93-58-3; ethyl 2-furoate, 614-99-3; (Z)-3-hexenyl hexanoate, 31501-11-8; (Z)-2-hexenyl hexanoate, 56922-79-3; ethyl benzoate, 93-89-0; (E)-2-hexenyl hexanoate, 53398-86-0; (E)-3-hexenyl hexanoate, 56922-82-8; ethyl phenylacetate, 101-97-3; 3-phenylpropyl acetate, 122-72-5; methyl (Z)-cinnamate, 19713-73-6; methyl (E)-cinnamate, 1754-62-7; ethyl (E)-cinnamate, 4192-77-2; cinnamyl acetate, 103-54-8; methyl hexadecanoate, 112-39-0; 3-pentanone, 96-22-0; pentanal, 110-62-3; 1-penten-3-one, 1629-58-9; hexanal, 66-25-1; (Z)-2-pentenal, 1576-86-9; (E)-2-pentenal, 1576-87-0; (Z)-3-hexenal, 6789-80-6; 4-methylheptan-3-one, 6137-11-7; heptanal, 111-71-7; (E)-3-hexenal, 69112-21-6; (E)-2-hexenal, 6728-26-3; 3-octanone, 106-68-3; 1-octen-3-one, 4312-99-6; 6-methyl-5-hepten-2-one, 110-93-0; (E,E)-2,4-hexadienal, 142-83-6; 1-methyl-3-cyclohexene-1-carboxaldehyde, 931-96-4; (E)-2-octenal, 2548-87-0; (E,Z)-2,4-heptadienal, 4313-02-4; (E,E)-2,4-heptadienal, 4313-03-5; decanal, 112-31-2; benzaldehyde, 100-52-7; (E,E)-2,4-octadienal, 30361-28-5; (E,Z)-2,4-octadienal, 557-48-2; acetophenone, 98-86-2; (E)-2-decenal, 3913-81-3; (E,E)-2,4-nonadienal, 5910-87-2; carvone, 99-49-0; (Z,E)-2,4-decadienal, 5910-88-3; (E,E)-2,4-decadiene, 25152-84-5; 3-phenyl-2-propenal, 104-55-2; (Z)-theaspirane, 43126-21-2; (E)-theaspirane, 43126-22-3; 1-phenoxybutane, 1126-79-0; acetylpyrazine, 22047-25-2; 1,2-dimethoxybenzene, 91-16-7; (E)-2-hexenoic acid, 13419-69-7; 2-(methylthio)benzothiazole, 615-22-5; 2-butanol, 78-92-2; 2-pentanol, 6032-29-7; 1-butanol, 71-36-3; 1-penten-3-ol, 616-25-1; 1-pentanol, 71-41-0; (E)-2-pentanol, 1576-96-1; (Z)-2-pentanol, 1576-95-0; 1-hexanol, 928-97-2; (E)-3-hexenol, 928-97-2; (Z)-3-hexenol, 928-96-1; (E)-2-hexenol, 928-95-0; 1-octen-3-ol, 3391-86-4; 1-heptanol, 111-70-6; 1-octanol, 111-87-5; 4-terpinenol, 562-74-3; 3-decanol, 1565-81-7; (E)-2-octen-1-ol, 18409-17-1; 5-undecanol, 37493-70-2; 2-phenylethanol, 60-12-8; 3-phenylpropanol, 122-97-4; eugenol, 97-53-0; 1-tetradecanol, 112-72-1; cinnamyl alcohol, 104-54-1; 1-hexadecanol, 36653-82-4; 1-octadecanol, 112-92-5; 1-penten-3-one, 1629-58-9; (E)-2-butenal, 123-73-9; 2-methyl-4-pentenal, 5187-71-3; 2-methyltetrahydrofuran-3-one, 3188-00-9; 3-hydroxy-2-butanone, 513-86-0; 5,6-dihydro-2H-pyran-2-carboxaldehyde, 53897-26-0; 4-hydroxy-5-methyl-3(2H)-furanone, 19322-27-1; 3,4-dihydro-8-hydroxy-3-methyl-2-benzo-1H-pyran-1-one, 17397-85-2; vanillin, 121-33-5; 4-oxodihydro- $\beta$ -ionol, 52210-16-9; 2,5-dimethyl-4-hydroxy-3(2H)-furanone, 3658-77-3; methyl 4-hydroxybutanoate, 925-57-5; methyl nicotinate, 93-60-7; acetic acid, 64-19-7; butanoic acid, 107-92-6; hexanoic acid, 142-62-1; heptanoic acid, 111-14-8; octanoic acid, 124-07-2; nonanoic acid, 112-05-0; decanoic acid, 334-48-5; benzoic acid, 65-85-0; phenylpropanoic acid, 501-52-0; tetradecanoic acid, 544-63-8; cinnamic acid, 621-82-9; hexadecanoic acid, 57-10-3; methylpyrazine, 109-08-0; 2,3,5-trimethylpyrazine, 14667-55-1; 5-ethoxythiazole, 25115-63-3; benzothiazole, 95-16-9;  $\gamma$ -decalactone, 706-14-9; 2-pentylfuran, 3777-69-3.

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