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Volatile Components of Pineapple Guava

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Volatile components of pineapple guava (*Feihoa sellowiana* Berg) fruit were identified by gas chromatography–mass spectrometry. Major constituents were germacrene D, bicyclogermacrene, methyl benzoate, β-caryophyllene, (*Z*)-3-hexenyl benzoate, linalool, humulene, and 3-octanone. Of the 85 compounds identified, 47 were not previously reported in pineapple guava.

Intrigued by reports that guava species in Hawaii were major hosts for the Mediterranean fruit fly (Vargas et al., 1983a) and the oriental fruit fly (Vargas et al., 1983b), we decided to determine the composition of volatile compounds of pineapple guava. Presumably, gauva volatiles act as attractants for these fruit flies, so identification of the volatiles plus testing for attractancy could lead to recognition of compounds potentially useful in fruit fly lures.

Volatile constituents of the common guava (*Psidium guajava*, L.) have been extensively investigated. In a distillate from guava puree, 22 components—mostly alcohols and esters—were identified (Stevens et al., 1970). An additional 21 compounds were identified by GC–MS analysis of the headspace of volatiles obtained via high vacuum from partially freeze-dried guava puree (Torline and Ballschmieter, 1973). Comparison of the content of eight sesquiterpenes in the leaf essential oils from wild guava trees allowed classification into three main chemotypes (Smith and Siwatibau, 1975). Twelve terpene hydrocarbons from a dichloromethane extract of guava puree and the possible significance of these compounds as insect attractants were reported by Wilson and Shaw (1978). Shiota (1978) reviewed studies of guava fruit flavor and, in addition, analyzed volatile components of purees, peels, and leaves of guava by GC–MS, identifying 39 compounds. From an isopentane extract of a guava vacuum steam distillate, MacLeod and Gonzalez de Troconis (1982) also identified 39 compounds and evaluated their contribution to guava aroma. Volatiles from fresh guava fruit pulp obtained by vacuum distillation with subsequent solvent extraction when analyzed by GC, GC–MS, and GC/FTIR spectroscopy contained 154 identifiable compounds (Idstein and Schreier, 1985). Five of these were terpenes, but no sesquiterpenes were reported. In contrast, a study of the essential oil from guava fruit peels showed 7 terpenes and 10 sesquiterpenes as well as caryophyllene oxide among the 21 compounds definitely identified (Oliveros-Belardo et al., 1986). Relative amounts of aroma compounds (88) in two Egyptian guava cultivars were compared and the odors of many characterized (Askar et al., 1986).

Pineapple guava (*Feihoa sellowiana* Berg) fruit volatiles have also been of interest. Notable among the volatiles distilled from the fruit were methyl benzoate and ethyl benzoate, which provided much of the distinctive aroma (Hardy and Michael, 1970). Three other benzoate esters were among the 56 compounds found in a steam distillate of fruit of a New Zealand cultivar by Shiota et al. (1980). This group also compared the volatile compounds in steam distillates from guava, strawberry guava (*Psidium cattleianum* Sabine), and yellow guava (*Psidium cattleianum* Sabine var. lucidem Hort). Collected headspace volatiles from a New Zealand feihoa fruit contained 11 compounds, 2 of these not previously reported (Shaw et al., 1983). The GC analysis of essential oil of ripe feihoa fruit cultivated in Georgia (USSR) indicated more than 250 volatile components of which 47 were identified (Starodubtseva and Kharebava, 1986).

EXPERIMENTAL SECTION

Materials. Mature abscissed fruits from a *F. sellowiana* plant in Berkeley, CA, were collected and surface cleaned. Part of the collection was put into a plastic bag and stored at −30 °C. The remainder was allowed to stand overnight at room temperature before being extracted with acetone.

Acetone Extraction. Whole fruits (2000 g) were blended with distilled acetone in a Waring Blendor. The mixture was filtered, and the filter cake was rinsed with acetone before being reblended with fresh solvent. Combined extracts amounted to 7 L. Acetone was removed from the extract by distillation under reduced pressure, and the distilled acetone plus some volatile fruit com-

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Table I. Volatile Components of Pineapple Guava

		KI,[a] DB-1		KI,[a] DB-wax				KI,[a] DB-1		KI,[a] DB-wax	
	μg/g	exptl	ref	exptl	ref		μg/g	exptl	ref	exptl	ref
ethyl acetate[b-d]	0.11		600	879	882	(*Z*)-3-hexenyl hexanoate[b-d]	0.19	1362	1360	1651	1647
benzene[b,c]	0.10	643	644	937	937	unknown (alcohol?)	0.60	1368		1873	
2-pentanone[b,c]	0.01		658	971	975	α-ylangene	0.05	1368	1369	1480	1482
2-methylbutanol	0.03	720	718	1199	1204	α-copaene[b,d]	0.30	1373	1374	1488	1491
pentanol[b,c]	0.04	746	744		1247	β-bourbonene	0.34	1380	1381	1515	1518
(*E*)-3-hexenal[b]	0.01		771	1132	1132	β-cubebene	0.28	1385	1385	1534	1538
hexanal[b-d]	0.04	773	772	1075	1078	β-elemene[b,c]	0.26	1386	1386	1585	1587
3-hexanol	0.10	776	776	1189	1192	longifolene	0.33	1401	1402	1570	1568
ethyl butyrate[b-d]	0.31	781	780	1028	1028	α-gurjunene[b]	1.43	1407	1408	1526	1528
furfural[b,c]	0.02		800	1454	1456	β-caryophyllene[b,d]	4.91	1414	1415	1592	1594
(*E*)-2-hexenal[b-d]	0.48	824	823	1211	1215	β-copaene[b,c]	0.12	1423	1424		1590
(*Z*)-3-hexenol[b-d]	0.40	836	834	1376	1378	ethyl cinnamate (trans)[b,c]	0.12	1431	1431	2123	2130
heptanal[b]	0.01	876	875		1182	aromadendrene[b]	0.20	1435	1435		1607
2-heptanol[c]	0.05		882	1315	1318	unknown	0.31	1444		1630	
(*E*)-2-heptenal	0.27	928	927	1321	1320	humulene[b,d]	2.60	1447	1448	1665	1667
3-octanone[b,c]	2.33	964	964	1248	1251	alloaromadendrene[b]	0.79	1454	1456		1647
1,2,4-trimethylbenzene	0.06	979	978		1277	δ-muurolene	0.47		1468	1685	1688
3-octanol[c]	0.32	980	979	1390	1394	germacrene D[b]	7.70	1472	1474	1705	1708
ethyl hexanoate[b-d]	0.42	981	981	1228	1232	2-tridecanone	0.20		1476	1806	1808
myrcene[b-d]	0.01		981	1157	1160	β-selinene[b]	0.35	1478	1480	1714	1717
(*Z*)-3-hexenyl acetate[b-d]	1.05	987	985	1310	1315	ledene	2.05		1490	1690	1695
2-methylbutyl 2-methylpropionate[c]	0.04	1002	1002	1194	1196	bicyclogermacrene[b]	6.71	1488	1490	1730	1733
benzyl alcohol[c]	0.08	1006	1004	1870	1872	α-farnesene[b,c]	0.58	1495	1495	1742	1745
limonene[b,d]	0.02		1020	1196	1198	γ-cadinene[b]	0.15	1503	1504		1758
cis-β-ocimene[b-d]	0.15	1026	1026		1232	calamenene[b]	1.30	1507	1507	1828	1832
acetophenone[b]	0.10	1031	1031		1643	δ-cadinene[b]	1.73	1512	1513	1752	1756
trans-β-ocimene[b-d]	0.20	1037	1037	1245	1249	unknown ($C_{15}H_{24}$)	0.64	1522		1781	
octanol[b]	0.02	1054	1053	1553	1557	(*E*)-3-hexenyl benzoate (tentative)	0.06	1534		2104	
linalool oxide A	0.03	1056	1056		1442	(*Z*)-3-hexenyl benzoate	3.10	1542	1542	2119	2124
methyl benzoate[b,c]	5.08	1066	1066	1611	1616	epiglobulol	0.06	1548	1548		2011
2-nonanone[c,d]	0.04	1069	1070	1384	1387	hexyl benzoate[c]	0.07		1551	2076	2074
nonanal[b]	0.10	1082	1082	1388	1389	unknown	0.35	1553		2008	
linalool[b-d]	2.67	1083	1083	1541	1545	palustrol (tentative)	0.28	1557		1931	
2-methylbutyl 2-methylbutanoate	0.06	1089	1090		1279	2-heptyl benzoate	0.79	1562	1562	2029	2034
ethyl benzoate[b,c]	1.75	1143	1143	1656	1663	globulol	0.78	1570	1571		2075
terpinen-4-ol[b-d]	0.03	1160	1159		1600	viridiflorol	1.16	1578	1578		2083
(*Z*)-3-hexenyl butyrate[b-d]	0.22	1167	1167	1454	1459	ledol	0.38	1590	1590		2028
α-terpineol[b-d]	0.16	1170	1170		1695	unknown	0.13	1596		2148	
nerol[c]	0.02	1210	1209		1802	unknown	0.27	1612		2065	
geraniol[b-d]	0.20	1234	1234	1841	1849	spathulenol (tentative)	0.42	1618		2223	
2-undecanone[c]	0.41	1273	1273		1596	unknown	0.46	1625		2183	
(*E*,*E*)-deca-2,4-dienal[b]	0.05	1288	1287		1807	unknown ($C_{15}H_{26}O$)	1.39	1634		2230	
methyl (*E*)-2,6-octadienoate, 3,7-dimethyl[c]	0.08	1301	1301		1629	2-pentadecanone	0.07	1678	1679	2018	2020
						(*E*,*E*)-farnesol	0.20	1698	1699	2345	2354
δ-elemene	0.06	1333	1333		1470	mintsulfide (tentative)	0.03	1718			
methyl 4-methoxybenzoate[c]	0.27	1337	1337	2092	2088	benzyl benzoate[c]	0.22	1720	1723		2633
α-cubebene[b]	1.33	1346	1347	1454	1457	flavone	0.63	2148	2150		

[a] Experimental and reference Kovats indices. [b] Reported in common guava. [c] Reported in pineapple guava. [d] Reported in strawberry guava or yellow guava.

ponents were collected in a flask chilled by solid carbon dioxide. Distilled water was added to the extract residue, and vacuum steam distillation was conducted for 4 h. Distillation of the previously collected acetone through a packed column at atmospheric pressure removed most of it and left a watery solution of pineapple guava extract volatiles. This was added to the steam distillate. The mixture was saturated with salt and extracted with ether freed of hydroperoxide by treatment with ferrous sulfate solution. The ether solution was dried with anhydrous sodium sulfate and concentrated to 5 mL by distillation of ether.

Freeze-Drying. Ice collected from freeze-drying of pineapple guava fruit was thawed. The aqueous solution of volatiles was saturated with salt and extracted with distilled ether. The ether extract was dried by sodium sulfate and then concentrated by distillation of ether. Volatiles thus obtained were compared with volatiles obtained from the acetone extract so that artifacts present in the acetone extract volatiles could be recognized.

Gas Chromatography. Chromatographic separations were carried out with Hewlett-Packard 5830 gas chromatographs fitted with flame ionization detectors. DB-1 and DB-Wax 60 m × 0.32 mm fused silica columns (J & W Scientific) were employed. Operating conditions for the DB-1 column were as follows: head pressure 24 psi; temperature program 50 °C for 0.1 min, 50–250 °C at 4 °C/min and then 250 °C for 5 min. This column was used for most of the GC–MS identification work and Kovats index determinations. Operating conditions for the DB-Wax column were the same except the head pressure was 21.5 psi and the upper temperature limit was 230 °C. Measured amounts of dodecane were added to concentrates of volatiles in order to calculate yields.

Component Identification. Identifications were based on mass spectral data obtained with a Finnigan MAT 4500 gas chromatograph–mass spectrometer data system and were verified by Kovats index comparisons on the DB-1 column or DB-Wax column.

RESULTS AND DISCUSSION

Table I lists the volatile compounds identified in pineapple guava fruit, the quantities found, and the experimental and reference retention indices of the compounds on the DB-1 and DB-Wax columns. Each compound listed was identified by its mass spectrum obtained during a GC–MS run. The 85 compounds identified include 29 hydrocarbons, 20 alcohols, 18 esters, 8 aldehydes, 7 ketones, linalool oxide, mintsulfide, and flavone. Of these compounds, 47 had not previously been reported in pineapple

guava and 27 had not been reported in any guava species.

An array of sesquiterpenes accounts for 23 of the 29 hydrocarbons found. In total, these sesquiterpenes constitute about 53% of the volatiles. Germacrene D, bicyclogermacrene, and β-caryophyllene are present in the greatest amount. Isomerization of a portion of the germacrene D may account for the presence of δ- and γ-cadinene, γ-muurolene, β-bourbonene, and β-copaene (Yoshihara et al., 1969). Similarly, bicyclogermacrene may be transformed into ledene (=viridiflorene), alloaromadendrene, aromadendrene, and α-gurjunene (Tressl et al., 1983). Other hydrocarbons found were four monoterpenes, benzene, and 1,2,4-trimethylbenzene.

Of the 20 identified alcohols, five were terpenoid and seven sesquiterpenoid. In addition to linalool, several sesquiterpene alcohols were present in relatively high concentrations, most notably viridiflorol and globulol.

The mass spectra of the compounds tentatively identified as palustrol and spathulenol matched well published spectra of these compounds, but we did not have samples available to determine GC retention indices.

The seven benzoate esters and methyl 4-methoxybenzoate are distinctive for pineapple guava. Methyl benzoate and ethyl benzoate have been reported in guava, but they are there present in much lower concentration. An equivalent situation exists for 3-octanone. Its concentration in guava is one-tenth or less than that in pineapple guava.

A small amount of mintsulfide was found. Composition of the molecular ion was $C_{15}H_{24}S$ and the mass spectrum gave an excellent match with the published mass spectrum (Maurer and Hauser, 1983). Previously identified in a variety of plant families including Myrtaceae, this compound is presumably derived from germacrene D (Takahashi et al., 1981).

Eight entries in Table I are for compounds of unknown identity. An unknown was listed as a pineapple guava component if the same mass spectrum was found in both the DB-1 and DB-Wax GC–MS runs. Eleven unknowns with molecular composition $C_{18}H_{30}O$ (MW 262) were detected but are not included in the table. Their DB-1 retention indices are in the range 1750–2000, and most of them have prominent mass spectral fragments at 204 and 161.

Initial tests of attractancy of pineapple guava volatiles for fruit flies indicate that they are substantially attractive to the melon fly and oriental fruit fly but are only slightly attractive to the Mediterranean fruit fly. Further tests will be carried out to determine which compounds produce the effect.

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Registry No. Limonene, 138-86-3; *cis*-β-ocimene, 3338-55-4; acetophenone, 98-86-2; *trans*-β-ocimene, 3779-61-1; octanol, 111-87-5; linalool oxide A, 34995-77-2; methyl benzoate, 93-58-3; 2-nonanone, 821-55-6; nonanal, 124-19-6; linalool, 78-70-6; 2-methylbutyl 2-methylbutanoate, 2445-78-5; ethyl benzoate, 93-89-0; terpinen-4-ol, 562-74-3; (*Z*)-3-hexenyl butyrate, 16491-36-4; α-terpineol, 98-55-5; nerol, 106-25-2; geraniol, 106-24-1; 2-undecanone, 112-12-9; (*E*,*E*)-deca-2,4-dienal, 25152-84-5; methyl (*E*)-3,7-dimethyl-2,6-octadienoate, 1189-09-9; δ-elemene, 20307-84-0; methyl 4-methoxybenzoate, 121-98-2; α-cubebene, 17699-14-8; (*Z*)-3-hexenyl hexanoate, 31501-11-8; α-ylangene, 14912-44-8; ethyl acetate, 141-78-6; benzene, 71-43-2; 2-pentanone, 107-87-9; 2-methylbutanol, 137-32-6; pentanol, 71-41-0; (*E*)-3-hexenal, 69112-21-6; hexenal, 66-25-1; 3-hexanol, 623-37-0; ethyl butyrate, 105-54-4; furfural, 98-01-1; (*E*)-2-hexenal, 6728-26-3; (*Z*)-3-hexenol, 928-96-1; heptanal, 111-71-7; 2-heptanol, 543-49-7; (*E*)-2-heptenal, 18829-55-5; 3-octanone, 106-68-3; 1,2,4-trimethylbenzene, 95-63-6; 3-octanol, 589-98-0; ethyl hexanoate, 123-66-0; myrcene, 123-35-3; (*Z*)-3-hexenyl acetate, 3681-71-8; 2-methylbutyl 2-methylpropionate, 23412-21-7; benzyl alcohol, 100-51-6; epiglobulol, 88728-58-9; hexyl benzoate, 6789-88-4; palustrol, 5986-49-2; 2-heptyl benzoate, 6624-59-5; globulol, 489-41-8; viridiflorol, 552-02-3; ledol, 577-27-5; spathulenol, 6750-60-3; 2-pentadecanone, 2345-28-0; (*E*,*E*)-farnesol, 106-28-5; mint sulfide, 72445-42-2; benzyl benzoate, 120-51-4; flavone, 525-82-6; α-copaene, 3856-25-5; β-bourbonene, 5208-59-3; β-cubebene, 13744-15-5; β-elemene, 33880-83-0; longifolene, 475-20-7; α-gurjunene, 489-40-7; β-caryophyllene, 87-44-5; β-copaene, 18252-44-3; ethyl *trans*-cinnamate, 4192-77-2; aromadendrene, 72747-25-2; humulene, 6753-98-6; alloaromadendrene, 25246-27-9; δ-muurolene, 120021-96-7; germacrene D, 23986-74-5; 2-tridecanone, 593-08-8; β-selinene, 17066-67-0; ledene, 21747-46-6; bicyclogermacrene, 24703-35-3; α-farnesene, 502-61-4; γ-cadinene, 39029-41-9; calamenene, 483-77-2; δ-cadinene, 483-76-1; (*E*)-3-hexenyl benzoate, 75019-52-2; (*Z*)-3-hexenyl benzoate, 25152-85-6.

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