Volatile Components of Pawpaw Fruit (*Asimina triloba* Dunal.)

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Volatile components of pawpaw (*Asimina triloba* Dunal.) fruit were mainly ethyl esters (hexanoate, 50.2%; octanoate, 19.3%; butanoate, 8.5%; and decanoate, 1.3%) which were accompanied by methyl esters (butanoate, hexanoate, octanoate, geranate, decanoate, and farnesate). Butane-2,3-diol monoesters (butanoate, hexanoate, and octanoate) and 3-hydroxybutan-2-one (acetoin) esters (acetate, butanoate, hexanoate, and octanoate) were also detected, and these esters except 3-acetoxybutan-2-one were reported to be present in nature for the first time. In addition, the effect of fruit maturity on volatile aroma composition was examined.

INTRODUCTION

Pawpaw (*Asimina triloba* Dunal.) belongs to the family Annonaceae which contains about 130 genera and 2300 species (Yamagishi, 1979). The principal genera of the family are *Annona* and *Asimina*. The former includes comparatively common tropical fruit such as the sugar apple (custard apple, *A. squamosa* L.), cherimoya (*A. cherimola* Mill.), and soursop (*A. muricata* L.), but the latter includes only the pawpaw as a fruit tree (Yamagishi, 1979).

Fruit-bearing trees often have different names in each country cultivated. Since pawpaw means papaya (*Carica papaya* L.) in the British Oceania and Central America, pawpaw should not be confused with papaya (Ching and Yong, 1980).

Pawpaw is native to the eastern United States, where it is found frequently along stream banks from New York to Florida. It was introduced to Japan in the 19th century but was not accepted and developed as a commercial fruit-bearing tree. One reason is that the fruit had much too strong a flavor for Japanese tastes. Hence, pawpaw is not so common in modern Japan, even though ripe fruit may be sold in fruit shops in October.

Pawpaw fruit is usually oblong in shape and 5–15 cm in length (Hoshikawa, 1976). The skin color is deep green when unripe and turns yellow and then dark brown when mature. The aroma of pawpaw fruit is very powerful and reminiscent of the mixture of pineapple, bread, and butter. The strong aroma is similar to that from tropical fruit, though pawpaw grows in a temperate climate.

There is no report on the analysis of the volatile components from pawpaw fruit despite its very interesting aroma. In this study the composition of the volatile components was investigated and changes during fruit maturation were checked.

MATERIALS AND METHODS

Fruit. Unripe green pawpaw fruits were picked from trees grown in the yards of houses in Usa, Ohita, Japan, in September, and the fruits were placed in a cardboard box at 20–25 °C. The volatile components were isolated from the fruit at three different stages (unripe, ripe, and overripe).

Isolation of Volatiles. Two or three fruits were peeled and several large seeds removed. Fruit flesh (62–120 g) was put into a 1-L spherical flask with distilled hot water (400 mL, about 90 °C) and an internal standard (2 g of 0.001% tetradecane in pentane solution). By use of the modified simultaneous distillation and extraction (SDE) apparatus (Flath and Forrey, 1977), volatiles were extracted with a solvent mixture of distilled pentane (14 g) and dichloromethane (6 g) for 15 min. The extract was concentrated at atmospheric pressure as described previously (Shiota et al., 1988).

Gas Chromatography (GC). For gas chromatography a 30 m × 0.25 mm i.d. DB-1 fused silica capillary column (0.25-μm film thickness; J&W Scientific) was used. The column was installed in a Hewlett-Packard 5890A GC equipped with injection splitter (split ratio 1:120) and flame ionization detector. The oven temperature was programmed from 50 (5 min isothermal) to 240 °C at 3 °C/min. The temperatures of the injector and detector were 250 and 280 °C, respectively. Helium (1 mL/min) was used as a carrier gas. Injection volumn was 0.5 μL. Peak area percentages were calculated automatically with a Hewlett-Packard 3392A integrator.

Gas Chromatography–Mass Spectrometry (GC–MS). A Hitachi 663 GC was combined with a Hitachi M-80A mass spectrometer (electron impact mode) with a Hitachi M-0101 data processor. A 60 m × 0.25 mm i.d. DB-1 column (0.25-μm film thickness; J&W) was used. The temperature program was isothermal for 5 min at 75 °C and then raised to 240 °C at 3 °C/min. The temperature of the injector was 250 °C. The column outlet was inserted directly into the ion source block. The mass spectra were recorded at an ionization voltage of 20 eV at an ion source temperature of 180 °C and with a speed of 0.445 scan/s over a mass range m/z 35–350. Retention indices of compounds were calculated with the Hitachi M-0101 data processor on the basis of retention time of normal alkanes (C_6–C_{25}).

Identification of Components. Identification of components was confirmed by comparison of the experimental retention index and mass spectrum with that of an authentic reference standard. In the absence of matched reference spectra, samples of proposed compounds were obtained from reagent houses or synthesized if they were not available.

Acetate, Butanoate, Hexanoate, and Octanoate of 3-Hydroxybutan-2-one. The mixture of 3-hydroxybutan-2-one (30 g), pyridine (24.5 g), and pentane (50 mL) was cooled to 5–10 °C. Acid chloride was added dropwise to it, as the temperature was maintained. The mixture was allowed to stand overnight and then poured into water (50 mL) and extracted with pentane. The organic layer was washed with water and later with 1% cuprous sulfate solution for removing residue trace pyridine. The concentrated oil was distilled. Butanoate: bp 67–71 °C/3 mmHg; MS m/z (%) 71 (100), 43 (77), 115 (12), 41 (7), 45 (7), 114 (2). Hexanoate: bp 115–116 °C/15 mmHg; MS m/z (%) 99 (100), 43 (58), 71 (40), 143 (9), 100 (5), 88 (5), 41 (4), 45 (4), 55 (4). Octanoate: bp 115–120 °C/4 mmHg; MS m/z (%) 57 (100), 127 (91), 43 (19), 71 (7), 128 (7), 88 (5), 41 (5), 171 (5), 55 (4), 98 (4), 130 (4), 45 (3), 72 (3), 84 (3). In the preparation of acetate, acetic anhydride was used instead of acid chloride. Acetate: 78–84 °C/30 mmHg; MS m/z (%) 43 (100), 87 (19), 130 (3), 45 (2), 86 (2). For odor and taste evaluation all esters above were purified by silica gel column chromatography.

Monobutanoate, Monohexanoate, and Monooctanoate of Butane-2,3-diol. These esters were prepared as above, but the reaction products were not only monoesters but also diesters.

0021-8561/91/1439-1631$02.50/0

Monoesters were isolated by careful distillation, but small amounts of diesters accompanied them. Monobutanoate: bp 76–79 °C/4 mmHg; MS m/z (%) 71 (100), 43 (42), 45 (30), 72 (9), 73 (9), 89 (9), 116 (9), 88 (5), 55 (4), 101 (3). Monohexanoate: bp 115–130 °C/3 mmHg; MS m/z (%) 99 (100), 43 (44), 71 (37), 73 (30), 45 (26), 89 (21), 57 (19), 88 (19), 144 (19), 72 (14), 101 (9), 100 (8), 115 (7), 60 (5). Monoctanoate: bp 127–140 °C/4 mmHg; MS m/z (%) 57 (100), 127 (95), 73 (58), 45 (30), 89 (23), 43 (21), 88 (19), 55 (16), 72 (14), 101 (12), 172 (9), 41 (9). For odor and taste evaluation they were purified by silica gel chromatography.

(*E*),(*E*)-Farnesyl Butanoate, Hexanoate, and Octanoate. These sesquiterpenic esters were prepared from (*E*),(*E*)-farnesol (98%, Aldrich Chemical Co., 0.45 g), pyridine (0.17 g), and the corresponding acid chloride in the same manner as in the previous section. The esters obtained were purified by using a similar column chromatographic technique. The yields of (*E*),(*E*)-farnesyl butanoate, hexanoate, and octanoate obtained were 0.4, 0.4, and 0.5 g, respectively. Butanoate: MS m/z (%) 69 (100), 81 (35), 93 (34), 71 (33), 68 (26), 43 (16), 136 (16), 80 (12), 121 (9), 123 (9), 135 (9), 41 (5). Hexanoate: MS m/z (%) 69 (100), 68 (33), 81 (42), 93 (42), 99 (21), 136 (21), 80 (16), 43 (12), 107 (12), 135 (12), 121 (9), 123 (8), 71 (7), 95 (7), 41 (5), 55 (5), 119 (5), 161 (5), 189 (5). Octanoate: MS m/z (%) 69 (100), 93 (56), 81 (37), 68 (28), 57 (21), 80 (21), 121 (16), 127 (16), 135 (16), 95 (12), 123 (12), 119 (9), 122 (9), 109 (7), 161 (7), 189 (7), 41 (5), 43 (5), 55 (5).

Methyl Farnesate. This ester was prepared from farnesal (mixture of four isomers, Kuraray). Farnesal (22 g) was oxidized to farnesic acid with $AgNO_3$ (34 g) and NaOH (16 g). The acid was esterified with excess CH_3OH (50 mL) and *p*-TsOH (0.5 g) at 48 °C for a month. The mixture was treated in the usual manner. Methyl farnesate obtained was purified on a silica gel column. It consisted of four peaks on GC. The *E,E* isomer appeared at the last retention time and corresponded to the methyl farnesate detected in pawpaw volatiles. MS (m/z (%): 69 (100), 114 (28), 41 (23), 81 (19), 121 (14), 136 (5), 55 (2), 70 (2), 82 (2), 83 (2), 93 (2), 95 (2), 107 (2), 109 (2), 122 (2), 123 (2), 207 (2).

Ethyl (*Z*)- and (*E*)-Hex-4-enoate. The condensation product of diethyl malonate (Tokyo Kasei Kogyo) and but-2-enyl chloride (TKK) was saponified and decarbonated to obtain hex-4-enoic acid (mixture of *Z* isomer and *E* isomer) in the usual manner. From this acid ethyl hex-4-enoate was prepared with concentrated H_2SO_4 in ethanol solution. *Z* isomer: MS m/z (%) 68 (100), 69 (80), 55 (59), 41 (55), 71 (53), 60 (32), 88 (27), 97 (27), 142 (27), 67 (18), 43 (11), 96 (9), 73 (7), 39 (5), 42 (5), 53 (5), 61 (5), 70 (5), 99 (5), 112 (5), 114 (5). The mass spectrum of the *E* isomer resembled closely that of the *Z* isomer.

Methyl and Ethyl (*E*)-Oct-2-enoate. These esters were prepared by the esterification of oct-2-enoic acid (TKK) in concentrated H_2SO_4 and methanol or ethanol solution.

Methyl and Ethyl (*Z*)-Oct-4-enoate. Ethyl (*Z*)-oct-4-enoate was purchased from Oril S.A., Paris. The methyl ester was prepared from the ethyl ester in excess CH_3OH with CH_3ONa.

RESULTS AND DISCUSSION

Analysis of Volatiles. The volatiles obtained from ripe pawpaw fruit are reported in Table I. The principal components were ethyl esters (83.1%) and methyl esters (2.6%). The former included ethyl hexanoate (50.2%), octanoate (19.3%), butanoate (8.5%), and decanoate (1.3%). The latter were methyl butanoate, hexanoate, octanoate, geranate, decanoate, and farnesate. The composition of both types of ester depended on maturity of pawpaw fruit. The ester in the highest concentration in the volatiles (ethyl hexanoate, 20 mg/kg) accounted for 50% of the fruit aroma.

The propyl (propyl butanoate and hexanoate) and butyl esters (butyl crotonate and octanoate) were also found in low concentration and are relatively uncommon in fruit aromas.

Esters of 3-Hydroxybutan-2-one and Butane-2,3-diol. The esters of 3-hydroxybutan-2-one (acetoin, I) and butane-2,3-diol (II) were detected, and some of them have not been found in fruit volatiles. The keto alcohol (I) is present in many dairy flavors but is not so common in

Table I. Volatile Aroma Compounds of Ripe Pawpaw Fruit

compd	peak area, %	RI exp[a]	RI auth[b]
ethyl acetate	0.29	600	590
3-hydroxybutan-2-one (acetoin)	0.73	680	672
methyl butanoate	0.04	706	703
methylcyclohexane	0.39	725	723
toluene	0.15	756	752
ethyl butanoate	8.47	784	780
ethyl (*E*)-but-2-enoate	0.59	820	815
(*Z*)-hex-3-en-1-ol	0.07	836	836
ethylbenzene	0.03	843	850
3-acetoxybutan-2-one (acetoin acetate)	0.12	855	856
styrene	}	878	880
unid	} 0.07	878	–
methyl hexanoate	0.57	907	907
ethyl hexanoate	50.22	996[c]	979
ethyl (*Z*)-hex-4-enoate	0.36	1009[c]	988
4-hexanolide (γ-hexalactone)	0.04	1015	1008
phenylacetaldehyde	0.02	1018	1012
2-ethylhexan-1-ol	0.04	1018	1012
limonene	0.13	1029	1024
butyl (*E*)-but-2-enoate	}	1024	1020
ethyl (*E*)-hex-2-enoate	} 0.19	1024	1019
3-[(propylcarbonyl)oxy]butan-2-one (acetoin butanoate)	1.32	1044	1038
ethyl hexa-2,4-dienoate	0.33	1070	–
ethyl (*E*),(*E*)-hexa-2,4-dienoate	0.08	1075	1072
butane-2,3-diol monobutanoate 1	0.49	1079	1076
propyl hexanoate	0.09	1082	1078
butane-2,3-diol monobutanoate 2	0.78	1088	1085
methyl (*Z*)-oct-4-enoate	0.01	1099	1092
ethyl 3-hydroxyhexanoate	0.92	1106	1104
methyl octanoate	1.83	1112	1112
ethyl (*Z*)-oct-4-enoate	0.13	1167	1164
ethyl octanoate	19.33	1192	1180
octanoic acid	+[d]	1209[c]	1158
ethyl nicotinate	0.04	1196	1190
citronellol	0.04	1211	1211
ethyl (*E*)-oct-2-enoate	0.02	1226	1224
3-[(pentylcarbonyl)oxy]butan-2-one (acetoin hexanoate)	1.11	1234	1233
butane-2,3-diol monohexanoate 1	0.51	1276	1272
butane-2,3-diol monohexanoate 2	0.86	1282	1277
methyl geranate	0.09	1305	1302
unid	0.08	1310	–
methyl decanoate	0.02	1313	1308
decanoic acid	0.36	1358	1353
butyl octanoate	0.02	1372	1371
ethyl decanoate	1.32	1383	1380
tetradecane (STD)[e]	0.79	1404	1400
3-[(heptylcarbonyl)oxy]butan-2-one (acetoin octanoate)	0.68	1435	1432
dodecan-1-ol	0.02	1460	1461
butane-2,3-diol octanoate 1	0.32	1473	1473
butane-2,3-diol octanoate 2	0.31	1477	1476
dodecanoic acid	0.19	1552	1561
diethyl phthalate	0.06	1556	1563
ethyl dodecanoate	0.55	1581	1578
tetradecan-1-ol	0.28	1663	1665
tetradecanoic acid	0.34	1748	1748
ethyl tetradecanoate	0.39	1777	1778
unid	0.06	1848	–
hexadecan-1-ol	0.35	1869	1872
dibutyl phthalate	0.21	1920	1923
unid	0.21	1927	–
hexadecanoic acid	0.80	1947	1956
ethyl hexadecanoate	0.11	1975	1979
total	97.93		

[a] Calculated automatically for the compounds detected in pawpaw fruit volatiles on the basis of retention index of alkanes (C_6–C_{25}). [b] Registered values for authentic compounds. [c] Unconfirmed value for broad peak. [d] Not calculated for broad peak. [e] Internal standard (0.32 mg/kg of fruit).

Table II. Odor and Taste Evaluation[a] of Selected Esters of 3-Hydroxybutan-2-one and Butane-2,3-diol

compd	taste in water	odor	purity[b]
3-acetoxybutan-2-one (acetoin acetate)	milky, soft, weak, sweet, buttery, melon-flesh-like (80 ppm[c])	powerful, ethereal, sweet, acetoin-like, yoghurt-like	99.17
3-[(propylcarbonyl)oxy]butan-2-one (acetoin butanoate)	buttery, fruity, creamy, estery, sweet, pear-like (80 ppm[c])	fruity, sweet, coarse, buttery, burnt-sugary	99.77
3-[(pentylcarbonyl)oxy]butan-2-one (acetoin hexanoate)	milky, fruity, oily, wet, fermented, fresh green, apple-like, pawpaw-like, reminescent of hard flesh (40 ppm[c])	fruity, pineapple-like, quince-like, reminiscent of hard flesh	99.46
3-[(heptylcarbonyl)oxy]butan-2-one (acetoin octanoate)	oily, juicy, fruity, spicy, powerful, pear-like, fermented (160 ppm[c])	oily, fermented	99.18
butane-2,3-diol monobutanoate	fruity, mild, succulent, weak, apple-like, muscat-like, Japanese-pear-like, walnut-like (40 ppm[c])	sweet-sour, succulent, fruity	96.29[d]
butane-2,3-diol monohexanoate	fruity, succulent, powerful, powdery, dusty, buttery, coarse, woody, rum-like, apple-peel-like, green (20 ppm[c])	buttery, succulent, fruity	95.40[d]
butane-2,3-diol monooctanoate	wet-fatty, weak, soft, cool, fresh-milk-like, blue-cheese-like, slightly astringent (20 ppm[c])	cool, milk-like, baked, bread-like	99.44[d]

[a] Evaluated by five expert panelists. [b] Peak area percentage using GC in the same condition of the volatile analysis. [c] Suitable concentration for taste evaluation. [d] Total of two peaks: butanoate (%) 87.06/9.23; hexanoate (%) 35.79/59.61; octanoate (%) 75.20/24.24.

fruit. The acetate of this alcohol (I) was reported to be in Arctic bramble (*Rubus arcticus* L.) which occurs in Finland (Kallio, 1976a,b). It was also detected in red wine aroma (Schreier, 1980) and has also been produced from thermal degradation of 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone (Shu et al., 1985). However, the butanoate, hexanoate, and octanoate of the alcohol (I) were detected in nature for the first time in this study. Each concentration of acetate, butanoate, hexanoate, and octanoate in the volatiles was of the same order of magnitude as that of the free alcohol (I).

Among various esters of the diol (II), three monoesters of butanoate, hexanoate, and octanoate were present in pawpaw volatiles. The diol (II) and its monoacetate were not detectable, perhaps because they are soluble in water. Compounds with two asymmetric carbons such as the monoesters of the diol (II) have theoretically two pairs of optical isomers. Therefore, the monoesters of the diol (II) will have two peaks on GC using a common stationary phase. Practically, they showed two peaks on the gas chromatogram of the pawpaw volatiles. The contents of these esters in the volatiles were 1.27% (butanoate), 1.37% (hexanoate), and 0.63% (octanoate). Total ester content (3.27%) of the diol (II) corresponded to that (3.23%) of the keto alcohol (I).

Both esters of the alcohol (I) and the diol (II) detected were especially important for pawpaw fruit aroma, because their odors were characteristic. The organoleptic evaluation of these compounds is shown in Table II. From these results the esters of the alcohol (I) would contribute to the unique esteric buttery character of pawpaw fruit aroma with a baked bread nuance. The esters of the diol (II) did not have a strong odor, but it was pleasantly mild, moist, with a ripe fruit nuance. They might contribute to the moist succulent fruity aroma character of pawpaw fruit.

Uncommon Esters. The esters of farnesol or farnesic acid have not been found in any fruits. Farnesol is a relatively common component in fruit flavor, but its esters have not been found. Farnesyl acetate, butanoate, hexanoate, and octanoate were detected in pawpaw fruit volatiles. This is the first report of these esters, except farnesyl acetate, from natural sources. On the other hand, among the esters of farnesic acid, only methyl farnesate was found in pawpaw aroma. This ester was reported to be present in the essential oils from roots of various species in the *Cyperus* genus (*C. iria, microiria, monophyllus, pilosus, rotundus*, and *serotinus*) (Iwamura et al., 1977, 1978a–c, 1979) grown in the wild in Japan. The farnesyl esters above and methyl farnesate have high boiling points and would not be expected to contribute to pawpaw fruit, but they might have a fixative effect on the fruit aroma.

Ethyl hexa-2,4-dienoate and nicotinate were also detected in the volatiles. Ethyl (*E*),(*E*)-hexa-2,4-dienoate (ethyl sorbate) was reported to be present in alcoholic beverages such as sparkling wine (De Rosa et al., 1983) and brandy (Ter Heide, 1977). Among fruit volatiles, this ester was detected only in carambola (starfruit) (Wilson et al., 1985) and banana (Drawert and Berger, 1983).

Ethyl nicotinate was present in alcoholic beverages such as ale (Barret, 1983), beer (Palamand, 1974), California brandy (Ough and Almy, 1986), and rum (Ter Heide, 1981). It was also present in jasmine flower oil (Toyoda et al., 1978) and iris rhizome oil (Garnero and Joulain, 1981). This ester strongly attracted an indigenous species of thrips (*Thrips obscuratus*) in New Zealand (Penman et al., 1982). As to fruit volatiles, ethyl nicotinate was found in carambola (Wilson et al., 1985), marula (*Sclerocarya birrea*) (Pretorius et al., 1985) grown in South Africa, and Arctic berries of *R. arctics* (Kallio, 1976a,b) and *R. arctics* subsp. *stellatus* (Kallio, 1975).

Acidic Components. Various carboxylic acids with even carbon numbers (C_4–C_{16} acids) were detected. Acid compounds, in general, are difficult to analyze by GC because their peaks are often broad and show so-called bleeding. Since peak area integration of acid compounds could not be calculated, they are shown qualitatively in Tables I and III. The acidic components are related closely with pawpaw fruit maturation.

Variation of Composition of Volatile Components with Fruit Maturity. Most tropical fruits and some fruits grown in a temperate climate are matured after picking. Pawpaw fruit is one such fruit. After picking, it ripens gradually at room temperature. Therefore, the effect of ripeness on aroma composition was examined at three different stages of maturity (unripe, ripe, and overripe). The results are shown in Table III.

The volatile compounds at the unripe stage consisted of a small amount of methyl esters and high boiling point acids. At maturity, there was a marked increase in volatile components, especially methyl and ethyl esters. The total amount of volatile components except acidic components was the highest at the ripe stage.

Table III. Volatile Aroma Compounds of Pawpaw Fruit at Different Maturity Stages

compd	μg/kg of fruit			RI[a]
	unripe	ripe	overripe	
ethyl acetate	8	143	108	
3-hydroxybutan-2-one (acetoin)	–[b]	227	3123	
methyl butanoate	–	119	47	
methylcyclohexane	63	95	196	
toluene	10	24	tr[d]	
ethyl butanoate	2	7109	2231	
ethyl (*E*)-but-2-enoate	–	95	291	
butyric acid	–	–	+[c]	
(*Z*)-hex-3-en-1-ol	–	12	41	
unid (4.98)[e]	–	36	446	
3-acetoxybutan-2-one (acetoin acetate)	–	24	108	
propyl butanoate	–	24	68	877 (876)
methyl hexanoate	–	5344	669	
unid (8.60)	–	24	–	
hexanoic acid	–	–	++[c]	
ethyl hexanoate	6	62864	29690	
ethyl (*Z*)-hex-4-enoate	–	60	352	
4-hexanolide (γ-hexalactone)	–	12	433	
limonene	27	36	548	
2-ethylhexan-1-ol	4	–	–	1015 (1012)
butyl (*E*)-but-2-enoate	–	24	845	
3-[(propylcarbonyl)oxy]butan-2-one (acetoin butanoate)	–	1193	2407	
ethyl hexa-2,4-dienoate	–	24	155	
ethyl (*E*),(*E*)-hexa-2,4-dienoate	–	tr	47	
butane-2,3-diol monobutanoate 1	–	143	473	
propyl hexanoate	–	167	–	
butane-2,3-diol monobutanoate 2	–	298	588	
methyl (*Z*)-oct-4-enoate	–	203	20	
ethyl 3-hydroxyhexanoate	–	83	676	
methyl octanoate	31	6179	791	
unid (18.22)	–	24	41	
methyl (*E*)-oct-2-enoate	–	36	–	
ethyl (*Z*)-oct-4-enoate	–	716	264	
unid (20.18)	–	167	88	
ethyl octanoate	20	24609	8781	
octanoic acid	–	+[c]	+++[c]	
ethyl nicotinate	–	36	–	
citronellol	–	24	–	1148 (1148)
4-octanolide (γ-octalactone)	–	24	–	1218 (1218)
3-[(pentylcarbonyl)oxy]butan-2-one (acetoin hexanoate)	–	1622	2609	
geraniol				1236 (1239)
butane-2,3-diol monohexanoate 1	–	489	331	
butane-2,3-diol monohexanoate 2	–	1121	831	
methyl geranate	–	215	453	
unid (26.42)	–	24	54	
methyl decanoate	–	107	tr	
decanoic acid	10	95	662	
butyl octanoate	–	48	34	
ethyl decanoate	3	1920	683	
3-[(heptylcarbonyl)oxy]butan-2-one (acetoin octanoate)	–	740	588	
butane-2,3-diol monooctanoate 1	–	230	81	
butane-2,3-diol monooctanoate 2	–	239	95	
methyl dodecanoate	–	60	tr	1506 (1509)
dodecanoic acid	12	24	135	
hexyl octanoate	–	tr	27	1565 (1567)
ethyl dodecanoate	tr	310	176	
tetradecan-1-ol	147	–	–	
(*E*),(*E*)-farnesol	–	48	115	1702 (1707)
methyl tetradecanoate				1705 (1708)
geranyl hexanoate	–	36	47	1731 (1731)
tetradecanoic acid	59	60	162	
methyl (*E*),(*E*)-farnesate	246	48	304	1764 (1761)
(*E*),(*E*)-farnesyl acetate	–	tr	–	1815 (1824)
ethyl tetradecanoate	–	215	115	
dibutyl phthalate	29	36	20	
geranyl octanoate	–	12	–	1923 (1923)
(*E*),(*E*)-farnesyl butanoate	–	tr	–	1990 (1988)
ethyl hexadecanoate	–	60	–	
hexadecanoic acid	130	–	230	
(*E*),(*E*)-farnesyl hexanoate	–	60	41	2181 (2181)
(*E*),(*E*)-farnesyl octanoate	–	36	41	2373 (2375)
total	807	118053	61361	

[a] Retention index, experimental (authentic); see footnote in Table I. [b] –, not detectable. [c] Not calculated for broad peak. [d] tr, trace. [e] Unidentified (retention time, min).

ACKNOWLEDGMENT

I thank Hajime Horie and Masataka Watanabe of Shiono Koryo Kaisha Ltd. for assistance in sampling pawpaw fruit. I am grateful to Dr. David A. Forss, New Zealand, for his review of the manuscript.

LITERATURE CITED

Barrett, J.; Halsey, S. A.; Peppard, T. L. Flavor Stability of Ales Brewed Using Hydrolyzed Maize Syrup. *J. Inst. Brew.* **1983**, *89*, 356–360.

Ching, H. F.; Yong, H. S. *Malaysian Fruits in Colour*; Tropical Press SDN BHD: Malaysia, 1980; p 17.

De Rosa, T.; Margheri, G.; Moret, I.; Scarponi, G.; Versini, G. Sorbic Acid as a Preservative in Sparkling Wine. Its Efficacy and Adverse Flavor Effect Associated with Ethyl Sorbate Formation. *Am. J. Enol. Vitic.* **1983**, *34*, 98–102.

Drawert, F.; Berger, R. G. *Z. Lebensm. Unters. Forsch.* **1983**, *176*, 275–280.

Flath, R. A.; Forrey, R. R. Volatile Components of Papaya (*Carica papaya* L., Solo Variety). *J. Agric. Food Chem.* **1977**, *25*, 103–108.

Garnero, J.; Joulain, D. New Constituents of Essential Oil of Iris Rhizomes. *Riv. Ital. EPPOS* **1981**, *63*, 141–145.

Hoshikawa, K. *Fruit*; Shibata Shoten: Tokyo, 1976; p 257.

Iwamura, J.; Kameda, J.; Komai, K.; Hirao, N. The Constituents of Essential Oils of *Cyperus serotinus* Rottb. and *Cyperus rotundus* L. *Nippon Kagaku Kaishi* **1977**, 1018–1020.

Iwamura, J.; Komaki, K.; Komai, K.; Hirao, N. The Constituents of Essential Oil from *Cyperus iria* L. *Nippon Nogei Kagaku Kaishi* **1978a**, *9*, 379–383.

Iwamura, J.; Kameda, M.; Komai, K.; Hirao, N. The Constituents of the Essential Oil from *Cyperus microiria* Steud. *Nippon Kagaku Kaishi* **1978b**, 1552–1555.

Iwamura, J.; Komaki, K.; Komai, K.; Hirao, N. The Constituents of Essential Oil from *Cyperus monophyllus* Vahl. *Nippon Nogei Kagaku Kaishi* **1978c**, *12*, 561–565.

Iwamura, J.; Komaki, K.; Komai, K.; Hirao, N. The Constituent of the Essential Oils of *Cyperus pilosus* Vahl. *Nippon Kagaku Kaishi* **1979**, 255–258.

Kallio, H. Chemical Constituents of the Volatile Aroma Compounds in *Rubus arcticus* L. subsp. *sellatus* (sm) Boivin with Reference to *Rubus arcticus* L. subsp. *arcticus*. *Ann. Univ. Turku, Ser. A2* **1975**, *57*, 60–68; *Chem. Abstr.* **1976**, *85*, 43747w.

Kallio, H. Identification of Vacuum Steam-Distilled Aroma Compounds in the Press Juice of Arctic Bramble, *Rubus arcticus* L. *J. Food. Sci.* **1976a**, *41*, 555–562.

Kallio, H. Development of Volatile Aroma Compounds in Arctic Bramble, *Rubus arcticus* L. *J. Food Sci.* **1976b**, *41*, 563–566.

Ough, C. S.; Almy, J. Some Volatile Trace Nitrogen Components in California Brandy *Am. J. Enol. Vitic.* **1986**, *37*, 137–140.

Palamand, S. R.; Gringsby, J. H. Stale Flavors in Beer. Identification of o-Aminoacetophenone and Ethyl Nicotinate in Beer *Brew. Dig.* **1974**, *49*, 58–59, 90.

Penman, D. R.; Osborne, G. F.; Worner, S. P.; Chapman, R. B.; McLaren, G. F. Ethyl Nicotinate: A Chemical Attractant for *Thrips obscuratus* (Thysanoptera:Thripidae) in Stonefruit in New Zealand *J. Chem. Ecol.* **1982**, *8*, 1299–1303.

Pretorius, V.; Rohwer, E.; Rapp, A.; Holtzhausen, L. C.; Mandery, H. Volatile Flavour Components of Marula Juice *Z. Lebensm. Unters. Forsch.* **1985**, *181*, 458–461.

Schreier, P. Wine Aroma Composition: Identification of Additional Volatile Constituents of Red Wine *J. Agric. Food Chem.* **1980**, *28*, 926–928.

Shiota, H.; Young, H.; Paterson, V. J.; Irie, M. Volatile Aroma Constituents of Pepino Fruit *J. Sci. Food Agric.* **1988**, *43*, 343–354.

Shu, C. K.; Mookherjee, B. D.; Ho, C. T. Volatile Components of the Thermal Degradation of 2,5-Dimethyl-4-hydroxy-3(2H)-furanone *J. Agric. Food Chem.* **1985**, *33*, 446–448.

Ter Heide, R.; De Valois, P. J.; Visser, J.; Jaegers, P. P.; Timmer, R. *Anal. Foods Beverages* **1978**, 249–281; *Chem. Abstr.* **1978**, *89*, 105833q.

Ter Heide, R.; Schaap, H.; Wobben, H. J.; De Valois, P. J.; Timmer, R. Flavor Constituents in Rum *Qual. Foods Beverages: Chem. Technol.* **1981**, *1*, 183–200; *Chem. Abstr.* **1982**, *96*, 18607v.

Toyoda, T.; Muraki, S.; Yoshida, T. Pyridine and Nicotinate Derivatives in Jasmin. *Agric. Biol. Chem.* **1978**, *42*, 1901–1905.

Wilson, C. W., III; Shaw, P. E.; Knight, R. J., Jr.; Nagy, S.; Klim, M. Volatile Constituents of Carambola (*Averrhoa carambola* L.) *J. Agric. Food Chem.* **1985**, *33*, 199–201.

Yamagishi, T.; Inoue, H.; Iwatsuki, K.; Kashiya, H.; Tamura, M.; Miura, K. *Syokubutsu Keito Bunrui no Kiso*; Hokuryukan: Tokyo, 1979; p 221.

Received for review December 11, 1990. Accepted May 20, 1991.

Registry No. Ethylbenzene, 100-41-4; styrene, 100-42-5; phenylacetaldehyde, 122-78-1; ethyl (*E*)-hex-2-enoate, 27829-72-7; ethyl (*E*)-oct-2-enoate, 7367-82-0; dodecan-1-ol, 112-53-8; diethyl phthalate, 84-66-2; hexadecan-1-ol, 36653-82-4; ethyl acetate, 141-78-6; 3-hydroxybutan-2-one, 513-86-0; methyl butanoate, 623-42-7; methylcyclohexane, 108-87-2; toluene, 108-88-3; ethyl butanoate, 105-54-4; ethyl (*E*)-but-2-enoate, 623-70-1; butyric acid, 107-92-6; (*Z*)-hex-3-en-1-ol, 928-96-1; 3-acetoxybutan-2-one, 4906-24-5; propyl butanoate, 105-66-8; methyl hexanoate, 106-70-7; hexanoic acid, 142-62-1; ethyl hexanoate, 123-66-0; ethyl (*Z*)-hex-4-enoate, 34495-73-3; 4-hexanolide, 695-06-7; limonene, 138-86-3; 2-ethylhexan-1-ol, 104-76-7; butyl (*E*)-but-2-enoate, 591-63-9; 3-[(propylcarbonyl)oxy]butan-2-one, 84642-61-5; ethyl hexa-2,4-dienoate, 110318-09-7; ethyl (*E*),(*E*)-hexa-2,4-dienoate, 2396-84-1; butane-2,3-diol monobutanoate, 59517-17-8; propyl hexanoate, 626-77-7; methyl (*Z*)-oct-4-enoate, 21063-71-8; ethyl 3-hydroxyhexanoate, 2305-25-1; methyl octanoate, 111-11-5; methyl (*E*)-oct-2-enoate, 7367-81-9; ethyl (*Z*)-oct-4-enoate, 34495-71-1; ethyl octanoate, 106-32-1; octanoic acid, 124-07-2; ethyl nicotinate, 614-18-6; citronellol, 106-22-9; 4-octanolide, 104-50-7; 3-[(pentylcarbonyl)oxy]butan-2-one, 134782-31-3; geraniol, 106-24-1; butane-2,3-diol monohexanoate, 95200-55-8; methyl geranate, 1189-09-9; methyl decanoate, 110-42-9; decanoic acid, 334-48-5; butyl octanoate, 589-75-3; ethyl decanoate, 110-38-3; 3-[(heptylcarbonyl)oxy]butan-2-one, 92038-24-9; butane-2,3-diol monooctanoate, 134782-32-4; methyl dodecanoate, 111-82-0; dodecanoic acid, 143-07-7; hexyl octanoate, 1117-55-1; ethyl dodecanoate, 106-33-2; tetradecan-1-ol, 112-72-1; (*E*),(*E*)-farnesol, 106-28-5; methyl tetradecanoate, 124-10-7; geranyl hexanoate, 10032-02-7; tetradecanoic acid, 544-63-8; methyl (*E*),(*E*)-farnesate, 3675-00-1; (*E*),(*E*)-farnesyl acetate, 4128-17-0; ethyl tetradecanoate, 124-06-1; dibutyl phthalate, 84-74-2; geranyl octanoate, 134782-33-5; ethyl hexadecanoate, 628-97-7; hexadecanoic acid, 57-10-3; (*E*),(*E*)-farnesyl hexanoate, 134782-34-6; (*E*),(*E*)-farnesyl octanoate, 134782-35-7; farnesal, 19317-11-4; farnesic acid, 7548-13-2; ethyl (*E*)-4-hexenoate, 34495-74-4.