Volatile Constituents of Green and Ripened Pineapple (*Ananas comosus* [L.] Merr.)

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Volatile constituents of green and ripened pineapples were isolated and identified by gas chromatography and gas chromatography/mass spectrometry. The numbers of volatiles found were 144 and 127 in green and ripened pineapples, respectively. Among a total of 157 constituents identified, 50 were identified for the first time from pineapple. Esters constituted over 80% of total volatiles from both green and ripened pineapples. The major volatile constituents in green pineapples were ethyl acetate and ethyl 3-(methylthio)propanoate. In ripened pineapples, ethyl acetate and butane-2,3-diol diacetate were the main constituents. Diastereoisomers of butane-2,3-diol diacetate were satisfactorily separated by a gas chromatographic chiral column.

Pineapple, one of the most popular tropical fruits in the world, has been cultivated in South America since the 15th century. However, it was not until the beginning of the 20th century that advanced canning technology made it possible to deliver green pineapple to people all over the world. People now enjoy the pineapple's unique sweet and sour flavor either as a green fruit or in processed form, such as in cake or pie.

Volatile constituents of pineapple have been investigated by many researchers. Numerous reviews on pineapple flavors have been published in the past two decades (Nicholas, 1973; Kishino and Kobayashi, 1981; Karg, 1983; Berger and Kollmannsberger, 1985; Engel et al., 1990). Nearly 200 volatile compounds have been reported from pineapple including alcohols, esters, aldehydes, ketones, and mono- and sesquiterpenoids. Recently, diastereomeric compounds began to be reported following the development of a gas chromatographic chiral column (Tressl et al., 1988). In the present study, volatile constituents of green and ripened pineapple were isolated and identified by gas chromatography and gas chromatography/mass spectrometry.

EXPERIMENTAL PROCEDURES

Materials. Pineapple fruit (*Ananas comosus* [L.] Merr.) imported from the Philippines was obtained from a local market. Authentic reference compounds were either purchased from commercial sources or synthesized in our laboratory. (*S,S*)-(+)-2,3- and (*R,R*)-(−)-2,3-butanediol diacetates were synthesized from corresponding butanediols by acetylation.

Reference Compounds. Ethyl and methyl 2-hydroxy-2(or 3)-methylbutanoate were prepared from esterification of commercially obtained 2-hydroxy-2-methylbutanoic acid (Aldrich Chemical Co., Milwaukee, WI). Methyl 3-hydroxy-2-methylbutanoate was prepared from methyl α-bromopropionate (Aldrich) and acetaldehyde according to established procedures (Rathke and Lindert, 1970). For ethyl 3-hydroxy-2-methylbutanoate, ethyl α-bromopropionate (Aldrich) was used instead of methyl α-bromopropionate. Acetoxy derivatives of ethyl- and methyl-2-hydroxy-2(or 3)-methylbutanoate, mono- and diacetate of butane-2,3-diol, and 3-acetoxy-2-butanone were obtained by reaction of the corresponding hydroxy esters, butane-2,3-diol, and 3-hydroxy-2-butanone with acetic anhydride, respectively. 2-Butyl-2-octenal was prepared by dimerization of hexanal via aldol condensation according to the method in Hauserman (1951). Ethyl and methyl-4-hydroxyoctanoate, ethyl 4-acetoxybutanoate, and ethyl 4-acetoxypentanoate were prepared from corresponding γ-lactones via 4-hydroxy esters, which were subsequently acetylated to obtain the corresponding 4-acetoxy esters according to the method in Mosandl and Gunther (1989).

Sample Preparation. After removal of the core and skin, pineapple flesh was cut into approximately 1-cm cubes (total weight, 1.1 kg) and homogenized with 600 mL of water and 210 mL of saturated NaCl solution. Solid materials were separated using a centrifuge, and 650 mL of water was added to the liquid layer. The sample was distilled at 32 °C under reduced pressure (35 mmHg), and approximately 950 mL of distillate was obtained. The distillate was extracted with 75 mL of dichloromethane using a liquid–liquid continuous extractor for 7 h. The solvent of extract was removed by distillation with a Vigreux column. The distillation was stopped when the volume of extract was reduced to 1 mL, and then the solvent was further removed under a nitrogen stream until the weight became 50 mg.

For a ripened fruit sample, the bottom of a pineapple was removed (approximately 3 cm) for allowing flesh to contact oxygen to increase the rate of ripening and allowed to stand for 3 days at room temperature. The ripened flesh was treated as described above.

Instrumental Analyses of Volatiles. All samples were analyzed with Kovats gas chromatographic retention index *I* (Kovats, 1965) and gas chromatography/mass spectrometry (GC/MS). The gas chromatographic retention index and MS fragmentation pattern of each component were compared with those of the authentic compound for qualitative analysis. A Shimadzu Model 9A gas chromatograph (GC) equipped with a 30 m × 0.25 mm i.d. DB-Wax bonded-phase fused-silica capillary column (J&W Scientific, Folsom, CA) and a flame ionization detector (FID) was used for routine quantitative analysis. The oven temperature was held at 40 °C for 10 min and then programmed to 200 °C at 2 °C/min.

A Shimadzu Model 7A GC equipped with a 30 m × 0.25 mm i.d. DB-Wax bonded-phase fused-silica capillary column (J&W Scientific) and a flame photometric detector (FPD) was used for analysis of sulfur-containing compounds. The oven temperature was programmed from 60 to 200 °C at 2 °C/min.

A Hewlett-Packard Model 5890 GC equipped with a 30 m × 0.25 mm i.d. Cyclodex-B bonded-phase fused-silica capillary column (J&W Scientific) and FID was used for analysis of optical isomers. The oven temperature was programmed from 40 to 200 °C at 2 °C/min.

For all GCs, the injector and detector temperatures were 250 °C. The injector split ratio was 30:1. The linear helium carrier gas flow rate was 30 cm/s.

A Varian 3500 GC equipped with a 30 m × 0.25 mm i.d. DB-Wax bonded-phase fused-silica capillary column (J&W Scientific)

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Table I. Volatile Compounds Found in Green and Ripened Pineapple

GC peak	compound	I^a	GC peak area% green	GC peak area% ripened	GC peak	compound	I^a	GC peak area% green	GC peak area% ripened
1	acetone	818	0.21	0.14	80	ethyl 3-(methylthio)propanoate	1558	10.38	3.23
2	methyl acetate	827	0.19	0.15	81	ethyl 3-acetoxy-2-methylbutanoate[b,e]	1563	2.56	1.51
3	ethyl acetate	884	24.45	33.49	82	*erythro*-3-acetoxy-2-butanol[b]	1563	*d*	*d*
4	ethyl propanoate	953	0.10	0.08	83	ethyl 3-hydroxy-2-methylbutanoate[b,e]	1563	1.27	1.57
5	propyl acetate	972	0.06	0.10	84	methyl 2-hydroxyhexanoate[b]	1574	0.09	0.07
6	methyl butanoate	984	0.28	0.14	85	ethyl 3-acetoxybutanoate	1576	1.32	1.46
7	methyl 2-methylbutanoate	1009	0.26	0.05	86	*threo*-3-acetoxy-2-butanol[b]	1576	0.55	0.86
8	2-methyl-2-butanol[b]	1011	0.26	*d*	87	2,5-dimethyl-4-methoxy-3(2*H*)-furanone	1584	0.61	0.35
9	2-methylpropyl acetate	1011	*c*	0.07	88	ethyl 3-hydroxypentanoate[b]	1587	*d*	*d*
10	ethyl butanoate	1032	0.37	0.15	89	ethyl 3-acetoxy-2-methylbutanoate[b,e]	1588	0.13	0.20
11	2-methyl-3-buten-2-ol	1036	0.16	0.05	90	ethyl 2-hydroxyhexanoate[b]	1592	0.06	0.06
12	ethyl 2-methylbutanoate	1048	0.04	0.03	91	4-terpineol	1596	0.02	*d*
13	hexanal	1077	*d*	*c*	92	γ-butyrolactone	1607	0.02	0.81
14	methyl pentanoate	1084	*d*	*c*	93	3-(methylthio)propyl acetate	1620	0.55	0.18
15	2-methylpropanol	1090	0.03	0.17	94	ethyl methyl succinate[b]	1631	*c*	0.05
16	3-methylbutyl acetate	1123	*d*	*d*	95	ethyl decanoate	1637	*d*	*d*
17	ethyl pentanoate	1131	*d*	*c*	96	menthol	1637	*d*	*d*
18	butanol[b]	1141	0.14	0.02	97	methyl 3-hydroxyhexanoate	1641	0.14	0.34
19	3-methyl-3-buten-2-ol[b]	1167	*d*	*c*	98	ethyl 3-acetoxypentanoate[b]	1647	*d*	*d*
20	methyl hexanoate	1183	0.50	0.11	99	2-butyl-2-octenal[b]	1659	*d*	*c*
21	limonene	1193	*d*	*d*	100	nonanol	1662	0.09	0.03
22	3-methylbutanol	1208	0.45	0.47	101	3-methylbutyric acid	1665	*d*	*d*
23	methyl 5-hexenoate	1226	*d*	*d*	102	2-methylbutyric acid	1666	*d*	*d*
24	ethyl hexanoate	1230	0.69	0.23	103	diethyl succinate[b]	1675	0.02	*c*
25	pentyl alcohol	1249	0.07	0.02	104	ethyl 3-hydroxyhexanoate	1675	5.95	6.44
26	3-methyl-2-butenyl acetate	1249	*d*	0.02	105	methyl 3-acetoxyhexanoate	1682	1.83	0.69
27	methyl (*Z*)-3-hexenoate	1253	*d*	*d*	106	γ-hexalactone	1682	1.40	1.91
28	2-methyltetrahydrofuran-3-one[b]	1259	*d*	*c*	107	α-terpineol	1692	*c*	*d*
29	methyl (*E*)-3-hexenoate	1259	*d*	*c*	108	ethyl 4-acetoxypentanoate[b]	1692	0.07	0.06
30	*p*-cymene	1262	*c*	*d*	109	3-(methylthio)propanol	1710	0.04	0.04
31	3-hydroxy-2-butanone (acetoin)	1276	4.40	8.74	110	ethyl 4-acetoxybutanoate[b]	1719	*d*	*d*
32	methyl 2-hydroxy-2-methylbutanoate[b]	1281	0.16	0.20	111	ethyl 3-acetoxyhexanoate	1719	8.67	6.58
33	methyl (*E*)-2-hexanoate	1284	*d*	*c*	112	methyl 4-acetoxyhexanoate	1726	0.25	0.47
34	hydroxyacetone[b]	1289	0.45	0.09	113	methyl phenylacetate	1749	*d*	*c*
35	ethyl (*Z*)-3-hexenoate	1292	*d*	*d*	114	ethyl 4-acetoxyhexanoate	1763	1.87	1.46
36	ethyl 2-hydroxy-2-methylbutanoate[b]	1301	0.52	0.42	115	methyl 5-acetoxyhexanoate	1766	1.03	1.48
37	ethyl (*E*)-3-hexenoate	1301	0.03	*d*	116	δ-hexalactone	1770	*d*	*c*
38	methyl lactate[b]	1314	*c*	0.03	117	ethyl phenylacetate	1776	0.04	*d*
39	*N,N*-dimethylformamide	1319	0.02	*c*	118	γ-heptalactone[b]	1784	0.06	0.05
40	3-methyl-2-butenol	1321	*c*	0.03	119	methyl 4-hydroxyhexanoate	1789	0.04	0.04
41	ethyl lactate	1339	*c*	0.08	120	ethyl 5-acetoxyhexanoate	1804	2.36	1.68
42	allyl isothiocyanate[b]	1353	*d*	*c*	121	methyl 3-hydroxyoctanoate	1807	*c*	*d*
43	hexanol	1353	0.10	0.06	122	ethyl 4-hydroxyhexanoate	1826	0.50	0.32
44	methyl 3-hydroxy-3-methylbutanoate[b]	1366	0.01	*d*	123	methyl 5-hydroxyhexanoate	1830	*d*	0.06
45	3-acetoxy-2-butanone[b]	1377	0.08	0.23	124	hexanoic acid	1841	0.33	0.12
46	(*Z*)-3-hexenol	1382	0.04	*d*	125	*p*-cymen-8-ol[b]	1843	0.04	*d*
47	methyl octanoate	1386	0.03	*c*	126	methyl 3-acetoxyoctanoate	1864	0.10	0.03
48	nonanal	1387	0.03	*c*	127	benzyl alcohol	1868	*d*	*c*
49	methyl (methylthio)acetate	1339	0.09	0.04	128	ethyl 5-hydroxyhexanoate	1872	0.14	0.12
50	ethyl 2-hydroxy-3-methylbutanoate[b]	1421	*d*	*d*	129	methyl 5-acetoxyheptanoate	1874	0.11	*d*
51	ethyl octanoate	1431	0.01	0.07	130	ethyl 3-hydroxyoctanoate[b]	1886	0.06	0.02
52	linalool oxide *cis*-furanoid	1438	*d*	*d*	131	methyl 4-acetoxyoctanoate	1892	*d*	0.03
53	ethyl (methylthio)acetate	1438	0.10	*d*	132	γ-octalactone	1898	1.13	0.03
54	methyl (*E,E*)-2,4-hexadienoate	1438	*d*	*c*	133	ethyl 3-acetoxyoctanoate	1898	0.15	0.42
55	acetic acid	1484	0.22	*c*	134	phenethyl alchol	1903	*c*	0.11
56	1-octen-3-ol[b]	1451	*d*	*c*	135	methyl 5-acetoxyoctanoate	1913	0.22	0.30
57	furfural	1451	*d*	*d*	136	ethyl 4-acetoxyoctanoate	1927	0.07	0.03
58	heptanol[c]	1456	0.03	*c*	137	δ-octalactone	1947	0.95	0.31
59	linalool oxide *trans*-furanoid	1461	*d*	*c*	138	ethyl 5-acetoxyoctanoate	1950	0.11	*c*
60	methyl 3-hydroxybutanoate	1475	0.10	0.04	139	methyl 4-hydroxyoctanoate[b]	1981	*c*	*d*
61	*erythro*-butane-2,3-diol diacetate[b]	1485	0.10	0.85	140	methyl 5-hydroxyoctanoate	1994	*d*	0.03
62	2-ethyl-1-hexanol	1491	0.11	0.02	141	phenol	1996	*d*	*c*
63	2-acetylfuran	1491	*d*	*c*	142	γ-nonalactone	2010	*d*	*c*
64	camphor	1499	*d*	*d*	143	ethyl 4-hydroxyoctanoate[b]	2014	*d*	0.07
65	dimethyl malonate	1506	0.30	0.18	144	4-hydroxy-2,5-dimethyl-3(2*H*)-furanone	2027	0.19	0.19
66	benzaldehyde	1506	*d*	*d*	145	ethyl 5-hydroxyoctanoate[b]	2030	0.05	0.02
67	ethyl 3-hydroxybutanoate[b]	1513	0.55	0.35	146	octanoic acid	2056	0.83	0.30
68	methyl 3-(methylthio)propanoate	1513	7.09	2.29	147	3-methylphenol	2081	*d*	*c*
69	methyl 3-hydroxy-2-methylbutanoate[b,e]	1518	*c*	0.08	148	γ-decalactone[b]	2127	*c*	*d*
70	*threo*-butane-2,3-diol diacetate[b]	1521	1.78	12.97	149	4-ethylphenol	2167	*c*	0.05
71	methyl 3-acetoxy-2-methylbutanoate[b,e]	1526	1.11	0.28	150	δ-decalactone	2174	0.05	0.02
72	methyl 3-hydroxy-2-methylbutanoate[b,e]	1534	0.08	0.03	151	ethyl hexadecanoate[b]	2254	*d*	*c*
73	methyl 3-acetoxybutanoate	1535	0.91	0.35	152	decanoic acid[b]	2269	0.09	0.03
74	propanoic acid	1535	0.26	0.12	153	γ-dodecalactone	2357	0.03	*d*
75	ethyl methyl malonate[b]	1539	0.30	0.13	154	5-(hydroxymethyl)furfural	2485	0.06	*c*
76	ethyl 3-hydroxy-2-methylbutanoate[b,e]	1544	0.13	0.16	155	diisobutyl phthalate	2526	0.04	0.03
77	linalool	1549	*d*	0.02	156	vanillin[b]	2538	*d*	*c*
78	methyl 3-hydroxypentanoate[b]	1552	*d*	*d*	157	dibutyl phthalate	2678	1.91	0.43
79	methyl 3-acetoxy-2-methylbutanoate[b,e]	1554	0.20	0.13					

[a] Kovats index. [b] Newly identified. [c] Not detected. [d] Peak area percent less than 0.02. [e] Diastereoisomers.

Table II. Mass Spectra of Newly Identified Compounds from Pineapples

compound	MW	m/z (%)
2-butyl-2-octenal	182	41 (100), 55 (98), 39 (56), 67 (48), 83 (48), 93 (48), 111 (45)
3-acetoxy-2-butanone	130	43 (100), 131 (7, M + 1), 42 (3), 45 (3), 44 (3), 71 (2)
erythro-3-acetoxy-2-butanol[a]	132	43 (100), 45 (41), 73 (29), 42 (7), 88 (6), 55 (5), 133 (4, M + 1)
threo-3-acetoxy-2-butanol[a]	132	43 (100), 45 (34), 73 (15), 88 (6), 42 (6), 55 (4), 133 (3, M + 1)
erythro-butane-2,3-diol diacetate[a]	174	43 (100), 115 (9), 72 (4), 45 (3), 42 (3), 44 (2)
threo-butane-2,3-diol diacetate[a]	174	43 (100), 115 (11), 72 (4), 42 (3), 45 (3), 44 (2), 39 (2)
ethyl 2-hydroxy-2-methylbutanoate	146	73 (100), 43 (62), 55 (52), 45 (14), 56 (10), 57 (9), 41 (7), 39 (6)
ethyl 2-hydroxy-3-methylbutanoate	146	73 (100), 55 (59), 76 (36), 43 (22), 41 (22), 39 (18), 45 (14)
ethyl 2-hydroxyhexanoate	160	69 (100), 41 (61), 43 (20), 39 (15), 87 (15), 57 (14), 45 (11)
ethyl 3-acetoxy-2-methylbutanoate[a]	188	43 (100), 102 (30), 83 (26), 74 (16), 44 (14), 55 (12), 56 (11)
ethyl 3-acetoxy-2-methylbutanoate[a]	188	43 (100), 102 (34), 83 (24), 74 (16), 55 (14), 56 (11), 44 (9)
ethyl 3-acetoxypentanoate	188	43 (100), 83 (27), 117 (14), 55 (12), 145 (8), 57 (8), 128 (5)
ethyl 3-hydroxy-2-methylbutanoate[a]	146	74 (100), 45 (46), 56 (60), 102 (59), 57 (42), 73 (39), 43 (37)
ethyl 3-hydroxy-2-methylbutanoate[a]	146	74 (100), 45 (69), 102 (65), 43 (60), 56 (59), 73 (45), 57 (37)
ethyl 3-hydroxybutanoate	132	43 (100), 45 (52), 45 (52), 42 (37), 71 (22), 60 (22), 87 (17), 117 (13)
ethyl 3-hydroxyoctanoate	188	43 (100), 117 (93), 71 (53), 41 (42), 55 (38), 189 (34, M + 1)
ethyl 3-hydroxypentanoate	146	43 (100), 71 (59), 117 (42), 59 (27), 89 (22), 60 (20), 44 (18)
ethyl 4-acetoxybutanoate	174	43 (100), 87 (41), 42 (22), 85 (14), 41 (13), 114 (9), 39 (8)
ethyl 4-acetoxypentanoate	188	43 (100), 101 (37), 55 (20), 99 (15), 42 (11), 56 (9), 39 (9)
ethyl 4-hydroxyoctanoate	188	85 (100), 41 (31), 57 (25), 39 (24), 55 (19), 45 (15), 43 (13)
ethyl 5-hydroxyoctanoate	188	99 (100), 71 (95), 43 (86), 41 (81), 55 (80), 42 (78), 88 (51)
methyl 2-hydroxyhexanoate	146	69 (100), 41 (77), 43 (42), 39 (22), 87 (15), 45 (13), 57 (10)
methyl 2-hydroxy-2-methylbutanote	132	43 (100), 73 (99), 55 (70), 45 (20), 57 (16), 41 (13), 56 (10)
methyl 3-acetoxy-2-methylbutanoate[a]	174	43 (100), 88 (27), 55 (12), 83 (12), 57 (10), 59 (10), 131 (5)
methyl 3-acetoxy-2-methylbutanoate[a]	174	43 (100), 88 (29), 57 (13), 55 (12), 83 (12), 59 (11), 56 (10)
methyl 3-hydroxy-2-methylbutanoate[a]	132	57 (100), 88 (79), 45 (53), 43 (40), 55 (35), 56 (35), 59 (27)
methyl 3-hydroxy-2-methylbutanoate[a]	132	57 (100), 88 (82), 45 (55), 56 (37), 43 (36), 55 (36), 59 (17)
methyl 3-hydroxy-3-methylbutanoate	132	43 (100), 59 (45), 85 (16), 117 (15), 74 (7), 42 (7), 40 (6), 41 (5)
methyl 3-hydroxypentanoate	132	43 (100), 71 (28), 103 (24), 44 (20), 59 (19), 61 (19), 74 (18)
methyl 4-hydroxyoctanoate	174	85 (100), 57 (42), 41 (37), 39 (28), 55 (21), 88 (18), 43 (16)
methyl tetrahydrofuran-3-one	100	43 (100), 72 (19), 45 (12), 42 (11), 57 (5), 100 (5)

[a] Diastereoisomers.

and interfaced to a Finnigan MAT Model 800 ion trap detector was used for MS identification of the GC components. The oven conditions for GC/MS were held at 50 °C for 2 min and then programmed to 200 °C at 2 °C/min.

RESULTS AND DISCUSSION

The yields of total volatiles (relative to the pineapple flesh used) were 0.0006% (w/w) from green pineapples and 0.0009% from ripened pineapples. Table I shows the compounds identified in green and ripened samples along with their GC peak area percent. Peak area percent of overlapped peaks, such as peaks 85 and 86, were calculated using a GC/MS total ion chromatogram (TIC). Among a total of 157 volatile compounds identified in the samples, 144 were found in green fruit and 127 were found in ripened fruit. Fifty compounds were identified for the first time from pineapple. Mass spectral data of some newly identified compounds in pineapple are shown in Table II. Some spectra showed a fragment resulting from self-chemical ionization in the ion trap detector; their fragments are shown as M + 1 in Table II (Eichelberger and Budde, 1987). Esters, which constituted 84% of total volatiles, were the most abundant volatiles found in green pineapple, followed by ketones (5.9%) and lactones (4.6%). These results are consistent with those of a previous study (Takeoka et al., 1989). Odor descriptions of some newly identified compounds are shown in Table III.

In green pineapples, the major volatile constituents were ethyl acetate (24.5%), ethyl 3-(methylthio)propanoate (10.4%), and ethyl 3-acetoxyhexanoate (8.7%). In ripened pineapples, ethyl acetate (33.5%), *threo*-butane-2,3-diol diacetate (13.0%), and 3-hydroxy-2-butanone (8.7%) were the major constituents. Engel et al. (1989) demonstrated that the concentrations of hydroxy and acetoxy acid esters increased during pineapple ripening. 3-Hydroxy-2-butanone has been reported as a main volatile constituent in a vacuum steam distillate from canned pineapple juice (Ohta et al., 1987). On the other hand, green pineapple contained it only in trace amounts (Takeoka et al., 1989). Formation of ethanol was not observed in the ripening process, suggesting that no fermentation occurred.

Table III. Odor Description of Some Newly Identified Compounds from Pineapple

compound	odor description[a]
2,3-butanediol diacetate	honey-like
ethyl 3-acetoxybutanoate	mint-like
ethyl 3-hydroxybutanoate	grape-like
ethyl 3-acetoxypentanoate	ripened pineapple-like
ethyl 3-acetoxy-2-methylbutanoate	pungent fruity
ethyl 3-hydroxy-2-methylbutanoate	grape-like, powdery
ethyl 3-hydroxypentanoate	fruity, pineapple-like
ethyl 3-hydroxyoctanoate	apple-like
methyl 2-hydroxy-2-methylbutanoate	woody
methyl 3-hydroxy-2-methylbutanoate	woody
methyl 3-acetoxy-2-methylbutanoate	burnt
ethyl 4-acetoxybutanoate	sour yogurt-like
ethyl 4-hydroxyoctanoate	milk-like
ethyl 2-hydroxyhexanoate	ripened pineapple-like
3-acetoxy-2-butanone	sour
ethyl 4-acetoxypentanoate	pineapple-like
methyl 3-hydroxypentanoate	honey-like
ethyl 2-hydroxy-2-methylbutanoate	grape-like
ethyl 2-hydroxy-3-methylbutanoate	ripened pineapple-like
methyl 5-hydroxyhexanoate	smoky tobacco-like, woody

[a] The descriptive analysis was done with an aqueous solution of each compound at the level of 1–10 ppm.

Among many hydroxy esters and acetoxy esters identified in the present study, 20 hydroxy esters (such as methyl or ethyl 3-hydroxy-2-methylbutanoate, methyl or ethyl 2-hydroxy-2-methylbutanoate, methyl 3-hydroxy-3-methylbutanoate, and ethyl 2-hydroxy-3-methylbutanoate) and 8 acetoxy esters (such as methyl or ethyl 3-acetoxy-2-methylbutanoate) were found for the first time in pineapple fruits. Moreover, these compounds apparently have never been reported in any other fruit.

Butane-2,3-diol diacetate, found in all samples, is a new

constituent of pineapples, and its precursor, 3-acetoxy-2-butanol, was also detected in trace amounts in the present study. Takeoka et al. (1989) reported 2,3-butanediol from pineapples, but they did not find its acetate derivative. Butane-2,3-diol diacetate has erythro and threo forms and a metho-form diastereoisomer. Therefore, it produces two peaks on a gas chromatogram. The retention index of the second peak (peak 70) matched that of the authentic (*S,S*)-(+)-, or (*R,R*)-(−)-butane-2,3-diol diacetate, suggesting that this peak is *threo*-butanediol diacetate; similarly, peak 61 is *erythro*-butanediol diacetate. Kovats indices of authentic (*R,S*)-, (*S,R*)-, (*S,S*)-(+)-, and (*R,R*)-(−)-butane-2,3-diol diacetates measured on a chiral column (permethylated β-cyclodextrin) were 1170, 1170, 1188, and 1200, respectively. The Kovats index of butane-2,3-diol diacetate in the pineapple samples was exactly the same as that of the authentic (*S,S*)-(+) form (1188). The (*R,R*)-(−) form was not detected, suggesting that (*S,S*)-(+)-butanediol diacetate is present in ripened pineapple as one of the major constituents (13%).

In addition to butane-2,3-diol diacetate, 3-hydroxy-2-butanone (acetoin) was found in ripened pineapple in large amounts.

Among sulfur-containing compounds identified, ethyl 3-(methylthio)propanoate and methyl 3-(methylthio)propanoate, which are known to have a characteristic pineapple flavor, were found as major constituents in the present study. Takeoka et al. (1991) reported several sulfur-containing esters which are similar to the major esters found in pineapple. The amounts of these compounds reduced as ripening progressed. In addition to seven sulfur-containing compounds detected by FID, four more were detected by FPD. Their structures have yet not been elucidated.

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Registry No. Hexanal, 66-25-1; methyl pentanoate, 624-24-8; ethyl pentanoate, 539-82-2; 3-methyl-3-buten-2-ol, 10473-14-0; methyl octanoate, 111-11-5; nonanal, 124-19-6; methyl (*E,E*)-2,4-hexadienoate, 689-89-4; acetic acid, 64-19-7; 1-octen-3-ol, 3391-86-4; heptanol, 111-70-6; linalool oxide *trans*-furanoid, 34995-77-2; 2-acetylfuran, 1192-62-7; 2-butyl-2-octenal, 13019-16-4; diethyl succinate, 123-25-1; methyl phenylacetate, 101-41-7; δ-hexalactone, 823-22-3; benzyl alcohol, 100-51-6; ethyl 5-acetoxyoctanoate, 35234-25-4; phenol, 108-95-2; γ-nonalactone, 104-61-0; 3-methylphenol, 108-39-4; ethyl hexadecanoate, 628-97-7; 5-(hydroxymethyl)furfural, 67-47-0; vanillin, 121-33-5; 2-methylpropyl acetate, 110-19-0; methyl 3-hydroxy-2-methylbutanoate, 34293-67-9; ethyl methyl succinate, 627-73-6; α-terpineol, 98-55-5; methyl 3-hydroxyoctanoate, 7367-87-5; phenethyl alcohol, 60-12-8; methyl 4-hydroxyoctanoate, 101853-51-4; γ-decalactone, 706-14-9; 4-ethylphenol, 123-07-9; ethyl 2-hydroxy-3-methylbutanoate, 2441-06-7; ethyl 3-hydroxybutanoate, 5405-41-4; *threo*-butane-2,3-diol diacetate, 79297-93-1; methyl 3-acetoxy-2-methylbutanoate, 139564-42-4; ethyl 3-hydroxy-2-methylbutanoate, 27372-03-8; methyl 3-hydroxypentanoate, 56009-31-5; ethyl 3-acetoxy-2-methylbutanoate, 139564-43-5; ethyl 3-acetoxybutanoate, 27846-49-7; ethyl 3-hydroxypentanoate, 54074-85-0; ethyl 2-hydroxyhexanoate, 52089-55-1; ethyl 3-acetoxypentanoate, 27846-50-0; ethyl 4-acetoxypentanoate, 27846-52-2; ethyl 4-acetoxybutanoate, 25560-91-2; methyl 5-hydroxyhexanoate, 62593-13-9; ethyl 3-hydroxyoctanoate, 7367-90-0; ethyl 4-hydroxyoctanoate, 57753-66-9; 2-methyltetrahydrofuran-3-one, 3188-00-9; methyl (*E*)-3-hexenoate, 13894-61-6; methyl (*E*)-2-hexenoate, 13894-63-8; *N,N*-dimethylformamide, 68-12-2; allyl isothiocyanate, 57-06-7; *p*-cymene, 99-87-6; methyl lactate, 547-64-8; 3-methyl-2-butenol, 556-82-1; ethyl lactate, 97-64-3; methyl 2-hydroxy-2-methylbutanoate, 32793-34-3; ethyl 2-hydroxy-2-methylbutanoate, 77-70-3; 3-acetoxy-2-butanone, 4906-24-5; acetone, 67-64-1; methyl acetate, 79-20-9; ethyl acetate, 141-78-6; ethyl propanoate, 105-37-3; propyl acetate, 109-60-4; methyl butanoate, 623-42-7; methyl 2-methylbutanoate, 868-57-5; 2-methyl-2-butanol, 75-85-4; ethyl butanoate, 105-54-4; 2-methyl-3-buten-2-ol, 115-18-4; ethyl 2-methylbutanoate, 7452-79-1; 2-methylpropanol, 78-83-1; 3-methylbutyl acetate, 123-92-2; butanol, 71-36-3; methyl hexanoate, 106-70-7; limonene, 138-86-3; 3-methylbutanol, 123-51-3; methyl 5-hexenoate, 2396-80-7; ethyl hexanoate, 123-66-0; pentyl alcohol, 71-41-0; 3-methyl-2-butenyl acetate, 1191-16-8; methyl (*Z*)-3-hexenoate, 13894-62-7; 3-hydroxy-2-butanone, 513-86-0; hydroxyacetone, 116-09-6; ethyl (*Z*)-3-hexenoate, 64187-83-3; ethyl (*E*)-3-hexenoate, 26553-46-8; hexanol, 111-27-3; methyl 3-hydroxy-3-methylbutanoate, 6149-45-7; (*Z*)-3-hexenol, 928-96-1; methyl (methylthio)acetate, 16630-66-3; ethyl octanoate, 106-32-1; linalool oxide *cis*-furanoid, 5989-33-3; ethyl (methylthio)acetate, 4455-13-4; furfural, 98-01-1; methyl 3-hydroxybutanoate, 1487-49-6; *erythro*-butane-2,3-diol acetate, 17998-02-6; 2-ethyl-1-hexanol, 104-76-7; camphor, 76-22-2; dimethyl malonate, 108-59-8; benzaldehyde, 100-52-7; methyl 3-(methylthio)propanoate, 13532-18-8; methyl 3-acetoxybutanoate, 89422-42-4; propanoic acid, 79-09-4; ethyl methyl malonate, 6186-89-6; linalool, 78-70-6; ethyl 3-(methylthio)propanoate, 13327-56-5; *erythro*-3-acetoxy-2-butanol, 54927-98-9; methyl 2-hydroxyhexanoate, 68756-64-9; *threo*-3-acetoxy-2-butanol, 59699-26-2; 2,5-dimethyl-4-methoxy-3(2*H*)-furanone, 4077-47-8; 4-terpineol, 562-74-3; γ-butyrolactone, 96-48-0; 3-(methylthio)propyl acetate, 16630-55-0; ethyl decanoate, 110-38-3; menthol, 89-78-1; methyl 3-hydroxyhexanoate, 21188-58-9; nonanol, 143-08-8; 3-methylbutyric acid, 503-74-2; 2-methylbutyric acid, 116-53-0; ethyl 3-hydroxyhexanoate, 2305-25-1; methyl 3-acetoxyhexanoate, 21188-60-3; γ-hexalactone, 695-06-7; 3-(methylthio)propanol, 505-10-2; ethyl 3-acetoxyhexanoate, 21188-61-4; methyl 4-acetoxyhexanoate, 112059-09-3; ethyl 4-acetoxyhexanoate, 121308-81-4; methyl 5-acetoxyhexanoate, 35234-22-1; ethyl phenylacetate, 101-97-3; γ-heptalactone, 105-21-5; methyl 4-hydroxyhexanoate, 101853-52-5; ethyl 5-acetoxyhex-

anoate, 35234-24-3; ethyl 4-hydroxyhexanoate, 101853-50-3; hexanoic acid, 142-62-1; *p*-cymen-8-ol, 1197-01-9; methyl 3-acetoxyoctanoate, 35234-21-0; ethyl 5-hydroxyhexanoate, 20266-62-0; methyl 5-acetoxyheptanoate, 139564-44-6; methyl 4-acetoxyoctanoate, 60121-04-2; γ-octalactone, 104-50-7; ethyl 3-acetoxyoctanoate, 85554-66-1; methyl 5-acetoxyoctanoate, 35234-23-2; ethyl 4-acetoxyoctanoate, 121312-01-4; δ-octalactone, 698-76-0; methyl 5-hydroxyoctanoate, 101853-49-0; 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone, 3658-77-3; ethyl 5-hydroxyoctanoate, 75587-05-2; octanoic acid, 124-07-2; δ-decalactone, 705-86-2; decanoic acid, 334-48-5; γ-dodecalactone, 2305-05-7; diisobutyl phthalate, 84-69-5; dibutyl phthalate, 84-74-2.