Volatile Constituents of Kiwi Fruit (*Actinidia chinensis* Planch.)

Gary R. Takeoka, Matthias Güntert, Robert A. Flath, Robert E. Wurz, and Walter Jennings*

The volatile compounds of kiwi fruit (*Actinidia chinensis* Planch.) were isolated by vacuum distillation with subsequent continuous liquid–liquid extraction with trichlorofluoromethane. The extracts were analyzed by capillary gas chromatography and capillary gas chromatography–mass spectrometry. The identified volatiles included 11 carbonyls, 9 alcohols, 16 esters, 11 hydrocarbons, and 1 miscellaneous component. Of the 48 compounds identified, 27 are reported for the first time as kiwi fruit constituents. Lipid degradation products such as C_6 aldehydes and alcohols comprised over 90% of the total volatiles.

Kiwi fruit (*Actinidia chinensis* Planch.) are produced by a deciduous vine native to the Yantze River Valley of China. The oval globular fruit has a fuzzy brown skin that covers its green flesh filled with small, black edible seeds. Though the fruit is a successful commercial crop in both New Zealand and the United States (Luh and Wang, 1984), only two publications about kiwi fruit volatiles appear in the literature (Young et al., 1983; Young and Paterson, 1985). These researchers identified 27 compounds in kiwi fruit of the Hayward cultivar. Ethyl butanoate, hexanal, and (*E*)-2-hexenal were reported to be important components of kiwi fruit aroma. The main purpose of this study was to identify additional kiwi fruit constituents that may contribute to its delicate flavor.

EXPERIMENTAL SECTION

Sample Preparation. Kiwi fruit of the major commercial variety, Hayward, were obtained locally. The fruit was allowed to ripen at room temperature. The soluble solids content of the juice reached 16–17% upon ripening. After separation of the skin the pulp was gently blended in a Waring blender, taking care not to fracture the seeds. The blended pulp was immediately subjected to vacuum distillation.

Isolation of Volatiles. An aliquot of blended pulp (1.2 kg) was diluted with distilled water (700 mL) in a 3-L three-neck flask and vacuum distilled (25–30 °C (1 mmHg)). Distillation continued for 2.5–3 h, yielding approximately 500 mL of distillate that was collected in two liquid nitrogen cooled traps. At the end of the distillation the pulp residue had visibly browned. A total of 3.6 kg of fruit pulp was distilled in three batches. The distillates were combined and immediately frozen until use. The combined distillate was extracted in 250-mL batches for 20 h with 60 mL of Freon 11 (trichlorofluoromethane, bp 23.8 °C). The Freon 11 was distilled through a 120 × 1.3 cm glass distillation column, packed with Fenske helices, prior to use. Each extract was carefully concentrated to approximately 100 μL by distillation of solvent, using a Vigreux column (16 cm), and a maximum pot temperature of 30 °C.

Gas Chromatography. A Hewlett-Packard 5880A gas chromatography with an FID, equipped with a 60 m × 0.25 mm i.d. DB-WAX column (J & W Scientific; bonded polyethylene glycol phase) was employed. The column temperature was programmed as follows: 30 °C hold 2 min, to 38 °C at 1 °C/min, then to 180 °C at 2 °C/min. Hydrogen carrier gas was used at a flow rate of 1.5 mL/min (30 °C). The injector and detector were maintained at 225 °C. A modified injection splitter (J & W Scientific) was used at a split ratio of 1:30.

Gas Chromatography–Mass Spectrometry. A Finnigan MAT 4500 series quadrupole gas chromatograph/mass spectrometer/data system equipped with the same capillary column as in the GC analysis was used. Helium was employed as the carrier gas at 1.3 mL/min. Injector temperature was 220 °C, and the ion source temperature was 180 °C. The outlet end of the fused silica column was inserted directly into the ion source block, which was maintained at approximately 180 °C. The column temperature was programmed from 30 °C (2 min isothermal) to 38 °C at 1 °C/min and then to 180 °C at 3 °C/min.

A second mass spectrometer, VG ZAB (magnetic sector), was directly coupled with a Hewlett-Packard 5790A gas chromatograph, equipped with a 30 m × 0.32 mm DB-WAX column (J & W Scientific; bonded polyethylene glycol phase). The carrier gas was He at 2.3 mL/min. The injector and transfer line temperatures were 225 and 180 °C, respectively. The column temperature was programmed as follows: 30 °C (2 min isothermal), to 38 °C at 1 °C/min, then to 180 °C at 2 °C/min. Both instruments were operated in the electron-impact mode at an ionization voltage of 70 eV.

RESULTS AND DISCUSSION

Trichlorofluoromethane has been used successfully as a solvent to extract grape berries (Rapp et al., 1976) and wines (Rapp et al., 1985) because of its extraction selectivity and efficiency (Au-Yeung and MacLeod, 1981), its low boiling point, and low danger of artifact formation (Mandery, 1983). Furthermore, it is nontoxic, nonexplosive, nonflammable, and almost odorless. Despite these advantages, trichlorofluoromethane has not been used extensively in flavor research. It has been used recently to extract wood apple (MacLeod and Pieris, 1981) and plum (Ismail et al., 1981) constituents.

Table I lists the kiwi fruit volatiles identified in this study. Mass spectral identifications were verified by comparison with Kovats retention indices of authentic reference standards. When reference compounds were not available, identifications were considered tentative. In total, 11 carbonyls, 9 alcohols, 16 esters, 11 hydrocarbons, and 1 miscellaneous component were identified. Of the 48 compounds identified, 27 are reported for the first time as kiwi fruit constituents. The amount of total volatile material isolated (based on GC peak areas; assuming all response factors equal to 1) was in the range of 2–10 ppm of the fruit pulp. Quantitatively, peroxidation products of unsaturated fatty acids (Schreier, 1984; Frankel, 1982) dominate the volatiles profile. These products that con-

Department of Food Science and Technology (G.R.T., M.G., W.J.) and Department of Chemistry (R.E.W.), University of California, Davis, California 95616, and Western Regional Research Center, U.S. Department of Agriculture—ARS, Berkeley, California 94710 (R.A.F.).

0021-8561/86/1434-0576$01.50/0

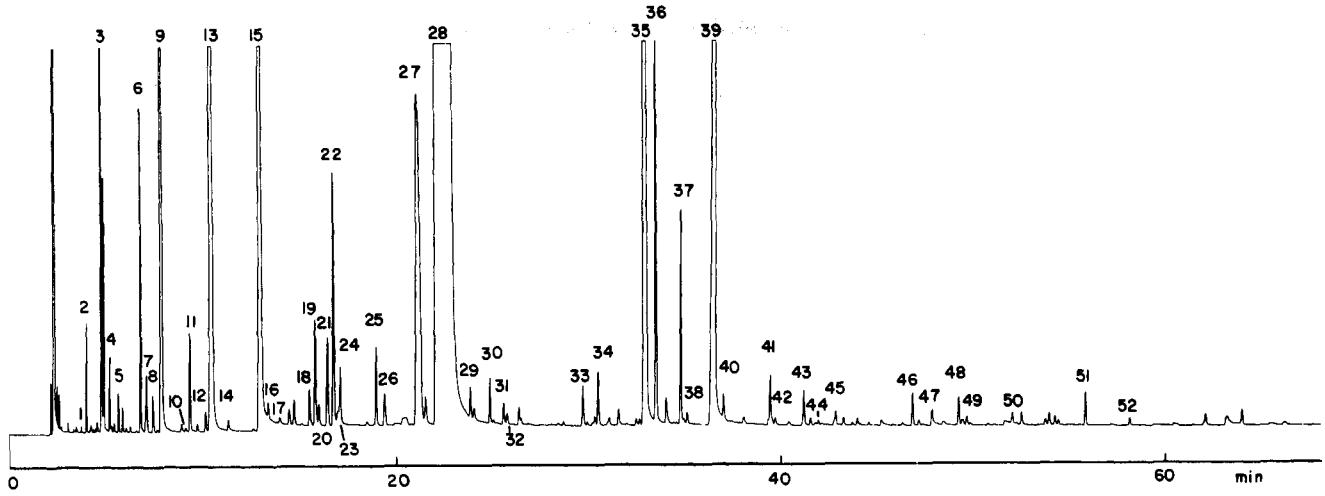

Figure 1. Capillary gas chromatogram of kiwi fruit volatiles obtained by vacuum distillation with subsequent solvent extraction (trichlorofluoromethane). Temperature programmed from 30 °C (2 min isothermal) to 38 °C at 1 °C/min and then to 180 °C at 2 °C/min on a 60 m × 0.25 mm i.d. DB-WAX column. The peak numbers correspond to the numbers in Table I.

Table I. Volatile Constituents of Kiwi Fruit

peak no.[f]	constituent	Kovats index DB-WAX	rel amt[c]	peak no.[f]	constituent	Kovats index DB-WAX	rel amt[c]
1	methyl acetate[a]	832	tr	27	((*Z*)-2-hexenal)[d]	(1196)[d]	0.87
2	tetrachloromethane[b]	850	0.04	28	(*E*)-2-hexenal	1210	77.87
3	ethyl acetate	890	0.72	29	ethyl hexanoate	1236	0.03
4	methyl propanoate	909	0.03	30	styrene[a]	1251	0.04
5	methyl 2-methylpropanoate	926	0.02	31	1-pentanol	1261	0.02
6	ethyl propanoate	961	0.19	32	*p*-cymene[a]	1263	0.01
7	ethyl 2-methylpropanoate	969	0.04	33	(*E*)-2-heptenal[a]	1317	0.03
8	pentanal	978	0.03	34	(*Z*)-2-pentenol[a]	1329	0.04
9	methyl butanoate	987	2.54	35	1-hexanol	1363	3.40
10	α-pinene[a]	1015	tr	36	(*E*)-3-hexenol	1370	0.32
11	1-penten-3-one	1020	0.07	37	(*Z*)-3-hexenol	1389	0.17
12	toluene[a]	1036	0.02	38	2,4-hexadienal[a]	1393	0.01
13	ethyl butanoate	1040	3.52	39	(*E*)-2-hexenol	1413	5.80
14	ethyl 2-methylbutanoate[a]	1056	0.01	40	((*Z*)-2-hexenol)[a,e]	1423	0.02
15	hexanal	1081	2.78	41	((*E,Z*)-2,4-heptadienal)[a,d]	(1461)[d]	0.03
16	methyl pentanoate	1087	0.01	42	1-heptanol[a]	1465	0.01
17	β-pinene[a]	1095	0.01	43	(*E,E*)-2,4-heptadienal[a]	1486	0.04
18	ethylbenzene[a]	1119	0.03	44	2-ethylhexanol[a]	1497	tr
19	(*E*)-2-pentenal	1124	0.09	45	benzaldehyde[a]	1512	0.02
20	*p*-xylene[a]	1127	0.02	46	methyl furoate[a]	1575	0.03
21	*m*-xylene[a]	1134	0.08	47	2,5-dimethyl-4-methoxy-3(2*H*)-furanone[a]	1591	0.01
22	(*E*)-3-hexenal[a]	1139	0.21	48	methyl benzoate	1613	0.02
23	Δ^3-carene[a]	1142	0.01	49	ethyl furoate[a]	1621	0.01
24	(*Z*)-3-hexenal[a]	1144	0.04	50	ethyl benzoate	1660	0.01
25	1-penten-3-ol	1170	0.07	51	naphthalene[a]	1725	0.03
26	*o*-xylene[a]	1176	0.03	52	methyl salicylate[a]	1765	0.01

[a] Identified for the first time in kiwi fruit. [b] Solvent contaminant. [c] Peak area percentage of total FID area excluding the solvent peak (assuming all response factors of 1). "tr" represents less than 0.01%. [d] Tentatively identified by mass spectral data only. [e] Tentatively identified by retention data only. [f] The peak numbers correspond to the numbers in Figure 1.

stitute over 90% of the total volatiles include (*E*)-2-hexenal (77.87%), (*E*)-2-hexen-1-ol (5.80%), 1-hexanol (3.40%), hexanal (1.78%), (*Z*)-2-hexenal (0.87%), (*E*)-3-hexen-1-ol (0.32%), (*Z*)-hex-3-enal (0.21%), and (*Z*)-3-hexen-1-ol (0.17%). The presence of large amounts of saturated and unsaturated aldehydes in the extract rendered it very sensitive to free-radical oxidation, particularly when concentrated for analysis. Extracts were therefore analyzed within 48 h after concentration and stored in liquid nitrogen or dry ice prior to analysis. Figure 1 shows a typical GC/FID chromatogram of kiwi fruit volatiles using a DB-WAX fused silica capillary column.

In the hydrocarbon group, the monoterpenes Δ^3-carene, β-pinene, and α-pinene were identified. The only terpene previously reported as a kiwi fruit constituent was limonene (Young and Paterson, 1985). The source of the aromatic hydrocarbons is unknown; some may arise from contamination during storage and handling of the fruit.

The presence of (*Z*)-2-pentenol is of interest. This uncommon plant volatile has been recently reported in cherimoya (Idstein et al., 1984) and guava (Idstein and Schreier, 1985) fruit. Ethanol, previously reported as a constituent of kiwi fruit (Young et al., 1983), was not found in the present study. This may have been produced by fermentation and may reflect differences in the quality of the samples used. Ethanol has been reported in stored or overripe mango but has not been found in the fresh ripe fruit (MacLeod and Snyder, 1985). It should also be noted that trichlorofluoromethane is not very effective at extracting ethanol from aqueous solution. This is not a

problem, for ethanol does not significantly contribute to flavor. Other constituents previously reported in kiwi fruit that were not found in this study include propyl butanoate, ethyl pentanoate, limonene, and methyl hexanoate. This apparent discrepancy may be related to the stage of ripeness of the fruit when sampled. Young and Paterson (1985) found that the level of kiwi fruit volatiles increased markedly during ripening and that the level of total volatiles (especially the esters) was much higher at the overripe stage than the ripe stage. They found propyl butanoate, ethyl pentanoate, limonene, and methyl hexanoate in overripe fruit but either could not detect or could detect only trace amounts in the ripe and underripe fruit.

Heterocyclic compounds found in kiwi fruit include methyl furoate, ethyl furoate, and 2,5-dimethyl-4-methoxy-3(2*H*)-furanone. The latter compound has been isolated from canned mango (Hunter et al., 1974) arctic bramble (Kallio, 1976), strawberries (Pyysalo et al., 1979), wild raspberries (Honkanen et al., 1980), pineapples (Pickenhagen et al., 1981), and cherimoya (Idstein et al., 1984). Attempts to isolate the corresponding hydroxylated compound 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone by direct extraction of the juice were unsuccessful.

ACKNOWLEDGMENT

We thank James Beutel for supplying the kiwi fruit used in this study. We are indebted to Wilhelm Pickenhagen (Firmenich SA), Ron Buttery (USDA, Berkeley), and Bedoukian Research, Inc., for providing various reference standards. M.G. thanks the Deutsche Gesellschaft fur Ernahrung, Frankfurt/Main (FRG), for their financial support.

Note Added in Proof. We discovered that we overlooked a previous publication about kiwi fruit volatiles by Haruyasu Shiota (*Karyo* **1982**, *137*, 59) while this paper was in press. Five of the compounds that we reported for the first time in kiwi fruit (α-pinene, toluene, *p*-cymene, methyl furoate, ethyl furoate) were previously reported by Dr. Shiota. He additionally found other constituents not reported by ourselves or in previous publications (Young and Patterson, 1985; Young et al., 1983). We regret this error and any inconvenience to Dr. Shiota.

Registry No. AcOMe, 79-20-9; AcOEt, 141-78-6; $EtCO_2Me$, 554-12-1; *i*-$PrCO_2Me$, 547-63-7; $EtCO_2Et$, 105-37-3; *i*-$PrCO_2Et$, 97-62-1; BuCHO, 110-62-3; $PrCO_2Me$, 623-42-7; $EtCOCH{=}CH_2$, 1629-58-9; PhMe, 108-88-3; $PrCO_2Et$, 105-54-4; *s*-$BuCO_2Et$, 7452-79-1; $BuCH_2CHO$, 66-25-1; $BuCO_2Me$, 624-24-8; EtPh, 100-41-4; (*E*)-$CHOCH{=}CHEt$, 1576-87-0; *p*-$Me_2C_6H_4$, 106-42-3; *m*-$Me_2C_6H_4$, 108-38-3; (*E*)-$CHOCH_2CH{=}CHEt$, 69112-21-6; (*Z*)-$CHOCH_2CH{=}CHEt$, 6789-80-6; $CH_2{=}CHCH(OH)Et$, 616-25-1; *o*-$Me_2C_6H_4$, 95-47-6; (*Z*)-$CHOCH{=}CHPr$, 16635-54-4; (*E*)-$CHOCH{=}CHPr$, 6728-26-3; $BuCH_2CO_2Et$, 123-66-0; $PhCH{=}CH_2$, 100-42-5; $BuCH_2OH$, 71-41-0; (*E*)-$CHOCH{=}CHBu$, 18829-55-5; (*Z*)-$HOCH_2CH{=}CHEt$, 1576-95-0; $HO(CH_2)_2Bu$, 111-27-3; (*E*)-$HO(CH_2)_2CH{=}CHEt$, 928-97-2; (*Z*)-$HO(CH_2)_2CH{=}CHEt$, 928-96-1; $CHO(CH{=}CH)_2Me$, 80466-34-8; (*E*)-$HOCH_2CH{=}CHPr$, 928-95-0; (*Z*)-$HOCH_2CH{=}CHPr$, 928-94-9; (*E,Z*)-$CHO(CH{=}CH)_2Et$, 4313-02-4; $HO(CH_2)_3Bu$, 111-70-6; (*E,E*)-$CHO(CH{=}CH)_2Et$, 4313-03-5; $HOCH_2CH(Et)Bu$, 104-76-7; PhCHO, 100-52-7; $PhCO_2Me$, 93-58-3; $PhCO_2Et$, 93-89-0; α-pinene, 80-56-8; β-pinene, 127-91-3; Δ^3-carene, 13466-78-9; *p*-cymene, 99-87-6; methyl furoate, 1334-76-5; 2,5-dimethyl-4-methoxy-3-(2*H*)-furanone, 4077-47-8; ethyl furoate, 1335-40-6; naphthalene, 91-20-3; methyl salicylate, 119-36-8.

LITERATURE CITED

Au-Yeung, C. Y.; MacLeod, A. J. *J. Agric. Food Chem.* **1981**, *29*, 502.
Frankel, E. N. *Prog. Lipid Res.* **1982**, *22*, 1.
Honkanen, E.; Pyysalo, T.; Hirvi, T. *Z. Lebensm. Unters. Forsch.* **1980**, *171*, 180.
Hunter, G. L. K.; Bucek, W. A.; Radford, T. *J. Food Sci.* **1974**, *39*, 900.
Idstein, H.; Herres, W.; Schreier, P. *J. Agric. Food Chem.* **1984**, *32*, 383.
Idstein, H.; Schreier, P. *J. Agric. Food Chem.* **1985**, *33*, 138.
Ismail, H. M.; Williams, A. A.; Tucknott, O. G. *J. Sci. Food Agric.* **1981**, *32*, 613.
Kallio, H. *J. Food Sci.* **1976**, *41*, 555.
Luh, B. S.; Wang, Z. *Adv. Food Res.* **1984**, *29*, 279.
MacLeod, A. J.; Pieris, N. M. *J. Agric. Food Chem.* **1981**, *29*, 49.
MacLeod, A. J.; Snyder, C. H. *J. Agric. Food Chem.* **1985**, *33*, 380.
Mandery, H. Dissertation, Universität Karlsruhe, FRG, 1983.
Pickenhagen, W.; Velluz, A.; Passerat, J.-P.; Ohloff, G. *J. Sci. Food Agric.* **1981**, *32*, 1132.
Pyysalo, T.; Honkanen, E.; Hirvi, T. *J. Agric. Food Chem.* **1979**, *27*, 19.
Rapp, A.; Hastrich, H.; Engel, L. *Vitis* **1976**, *15*, 29.
Rapp, A.; Güntert, M.; Ullemeyer, H. *Z. Lebensm. Unters. Forsch.* **1985**, *180*, 109.
Schreier, P. In *Chromatographic Studies of Biogenesis of Plant Volatiles*, Verlag: Heidelberg, 1984.
Young, H.; Paterson, V. J. *J. Sci. Food Agric.* **1985**, *36*, 352.
Young, H.; Paterson, V. J.; Burns, P. J. W. *J. Sci. Food Agric.* **1983**, *34*, 81.

Received for review November 4, 1985. Accepted March 4, 1986.