

Winter, M.; Malet, G.; Pfeiffer, M.; Demole, E. "Structure d'Une Lactone Odorante Presente dans l'Essence de Jasmin (*Jasminum grandiflorum* L.)". *Helv. Chim. Acta* 1962, 45, 1250-1253.

Yamanishi, T.; Kawatsu, M.; Yokoyama, T.; Nakatani, Y. "Methyl Jasmonate and Lactones Including Jasmine Lactone in Ceylon

Tea". *Agric. Biol. Chem.* 1973, 37, 1075-1078.

Received for review February 24, 1987. Revised manuscript received October 7, 1987. Accepted January 12, 1988. Names of products are included for the benefit of the reader and do not imply endorsement by USDA.

## Nectarine Volatiles: Vacuum Steam Distillation versus Headspace Sampling

Gary R. Takeoka,\*<sup>1</sup> Robert A. Flath, Matthias Güntert, and Walter Jennings

The volatile components of fresh, tree-ripened nectarines (*Prunus persica nectarina*) of the Flavortop variety were analyzed by capillary gas chromatography and gas chromatography-mass spectrometry. Samples were prepared by vacuum distillation of the fruit pulp and skin followed by continuous solvent extraction (trichlorofluoromethane-dichloromethane, 9:1, v/v). A total of 62 components were identified in the extract including 21 alcohols, 15 esters, 10 carbonyls, 2 acids, 1 hydrocarbon, and 13 miscellaneous components. Lactones and peroxidation products of unsaturated fatty acids (i.e., C<sub>6</sub> aldehydes and alcohols) were the major constituents of the extract. Headspace analysis of intact fruit yielded the identification of 99 components including 43 esters, 33 hydrocarbons, 10 alcohols, 6 carbonyls, and 7 miscellaneous components.

The nectarine (*Prunus persica nectarina*) is an important commercial crop in the United States. Most of the nectarines sold in the United States are produced in California with over 100 varieties grown commercially in the state. The origins of the fruit are not known, but its history dates back 2000 years and merges into that of the peach (LaRue and Gerdt, 1983). There is controversy over whether the nectarine is a separate and distinct fruit or merely a variety of peach. In contrast to the peach, nectarines lack the fuzz or pubescence of the skin.

Current commercial nectarine varieties are vastly different from varieties produced before World War II. By crossing them with peaches, today's nectarines are larger, firmer, and more highly colored than their forebears. They also have yellow flesh rather than the white flesh that characterized the older varieties.

Despite extensive studies on peach volatiles (van Straten and Maarse, 1983), there are few data on the volatile constituents of nectarine. Lim and Romani (1964) studied volatiles of ripening nectarine (Early Sun Grand variety) using direct headspace sampling but only identified ethylene. Our study was directed toward the identification of nectarine volatiles (Flavortop variety) using two different sampling methods. The Flavortop variety originated in Fresno, CA, and was developed by the U.S. Department of Agriculture. The cultivar was produced from an open-

pollinated seedling of the Fairtime peach (Brooks and Olmo, 1972). The large, ovate fruit possesses a predominantly red over amber skin. The bright yellow flesh is generally streaked throughout with red.

### EXPERIMENTAL SECTION

**Materials.** Fresh, tree-ripened nectarines (*P. persica nectarina*) of the Flavortop variety were obtained from a local orchard in Winters, CA (July-August 1985 and 1986). Ethanox antioxidant 330 was supplied by Ethyl Corp. (Baton Rouge, LA 70820). 3-Octyn-1-ol was obtained from Pfaltz & Bauer, Inc. (Waterbury, CT 06708).

**Sampling Techniques.** 1. *Vacuum Distillation-Extraction.* The fruit was washed with distilled water and allowed to air-dry. The fruit was cut in half, and the stones were removed and discarded. The skin and pulp were gently blended for 20 s in a Waring blender. The blended material was immediately subjected to vacuum distillation. A separate batch of nectarines was prepared in the same way except both the stones and skin were discarded and only the pulp was sampled.

An aliquot of blended pulp (0.6-0.7 kg) was diluted with distilled water (350 mL) in a 3-L three-neck flask and vacuum-distilled [33-35 °C (1 mmHg)]. The material had a tendency to foam but could be controlled by reducing the pressure gradually. After 2 h a second aliquot of blended fruit (0.6-0.7 kg) and distilled water (350 mL) was added. Distillation continued for an additional 2 h (4 h total), yielding approximately 500 mL of distillate which was collected in two liquid nitrogen cooled traps. A total of 3.9 kg of fruit pulp was distilled in three batches. The originally yellow pulp material was noticeably browned at the end of the distillation. 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) or Freon 11-dichloromethane (9:1, v/v; bp 23.8 °C). Since no nectarine volatiles coeluted with the dichloromethane peak,

Department of Food Science and Technology, University of California, 1480 Chemistry Annex, Davis, California 95616 (G.R.T., W.J.), Western Regional Research Center, U.S. Department of Agriculture—Agricultural Research Service, Albany, California 94710 (R.A.F.), and Haarmann & Reimer GmbH, Postfach 1253, D-3450 Holzminden, West Germany (M.G.).

<sup>1</sup> Present address: Western Regional Research Center, U.S. Department of Agriculture—Agricultural Research Service, Albany, CA 94710.

the Freon 11-dichloromethane mixture was used in the reported analyses. The Freon 11 and dichloromethane were purified before use by distillation through a 120 × 1.3 cm glass distillation column, packed with Fenske helices. Two milligrams of Ethanox antioxidant 330 [1,3,5-trimethyl-2,4,6-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzene] was added to each extract before being carefully concentrated with a Vigreux column (16 cm) to a final volume of approximately 100  $\mu$ L (pot temperature 30 °C).

**2. Dynamic Headspace Sampling. Headspace Sampling Apparatus.** The sampling chamber, activated charcoal air purifier, and sampling pump have been described before (Flath and Ohinata, 1982). The Tenax traps were constructed from 10.2-cm (4-in.) lengths of 0.95-cm ( $3/8$ -in.) o.d. stainless steel tubing, to one end of which was brazed a flared 3.2-cm-long stub of 0.64-cm ( $1/4$ -in.) o.d. tubing. The traps were loaded with ca. 0.7 g of 35/60-mesh Tenax GC (Alltech Associates, Deerfield, IL), held in place with fine stainless steel screens and slip rings. This provided a porous polymer column, 7-cm length × 0.86-cm o.d. The traps were closed with stainless steel Swagelok caps, using Teflon front ferrules. Traps were cleaned by heating them to ca. 250 °C for at least 2 h, while a low flow of purified helium (activated carbon and oxygen traps in series) was maintained through the trap in a reverse direction to that used for sample trapping. The traps were cooled to ambient temperature before removal from the gas flow.

**Headspace Sampling Procedure.** Three intact fruit (488 g) were placed in the sample chamber, and the system was purged for 17 h with a 50 mL/min flow of purified air. A clean Tenax trap was attached to the  $1/4$ -in. Swagelok exit port of the chamber, and the air stream was sampled for 30 min at 50 mL/min (1.5 L total). The first trap was then removed and capped, and a second clean trap was substituted. Sampling was repeated for a second 30-min period at 50 mL/min. The first trapped sample was examined by fused silica capillary/flame ionization detector gas chromatography (GC/FID), and the second was used for headspace capillary gas chromatography-mass spectrometry (GC-MS).

**Gas Chromatography.** A Hewlett-Packard 5880A gas chromatograph (Hewlett-Packard, Avondale, PA) with a flame ionization detector (FID), equipped with a 60 m × 0.25 mm (i.d.) DB-WAX column ( $d_f = 0.25 \mu\text{m}$ , bonded poly(ethylene glycol) phase, column A) was employed. The column temperature was programmed from 30 °C (2 min isothermal) to 180 °C at 2 °C/min. Hydrogen carrier gas was used at a flow rate of 1.42 mL/min (30 °C). The injector and detector were maintained at 240 °C. A modified injection splitter was used at a split ratio of 1:30. A 30 m × 0.25 mm (i.d.) DB-1 column ( $d_f = 0.25 \mu\text{m}$ , bonded dimethyl polysiloxane, column B) was also used. For column B the column temperature was programmed from 30 °C (2 min isothermal) to 150 °C at 2 °C/min and then to 250 °C at 4 °C/min. Hydrogen carrier gas was used at a flow rate of 1.52 mL/min (30 °C). The injector and detector were maintained at 250 °C. The fused silica columns and inlet splitter were obtained from J&W Scientific, Folsom, CA.

For the headspace studies, a Hewlett-Packard 5830A gas chromatograph fitted with an FID was used. A lab-constructed inlet system provided for thermal desorption/back-flushing of loaded Tenax traps. Volatiles were desorbed from the trap by heating from ambient temperature to 220 °C over 15 min. A helium flow of 15 mL/min was maintained through the trap during desorption. Desorbed

headspace volatiles were trapped in a liquid nitrogen chilled spiral stainless steel capillary trap, from which they were subsequently flash-transferred for GC/FID examination by removing the LN<sub>2</sub> bath and heating the spiral trap with a large heat gun. A 60 m × 0.32 mm (i.d.) DB-1 fused silica capillary column ( $d_f = 0.25 \mu\text{m}$ , bonded dimethyl polysiloxane, column C) was used for the separation. The column was operated at a constant head pressure of 20 psi (140 kPa) and was programmed from 0 to 225 °C at 3 °C/min. Peak area percent values provided by the HP 5830A were used directly for indication of the relative amounts of individual components, without response factor correction.

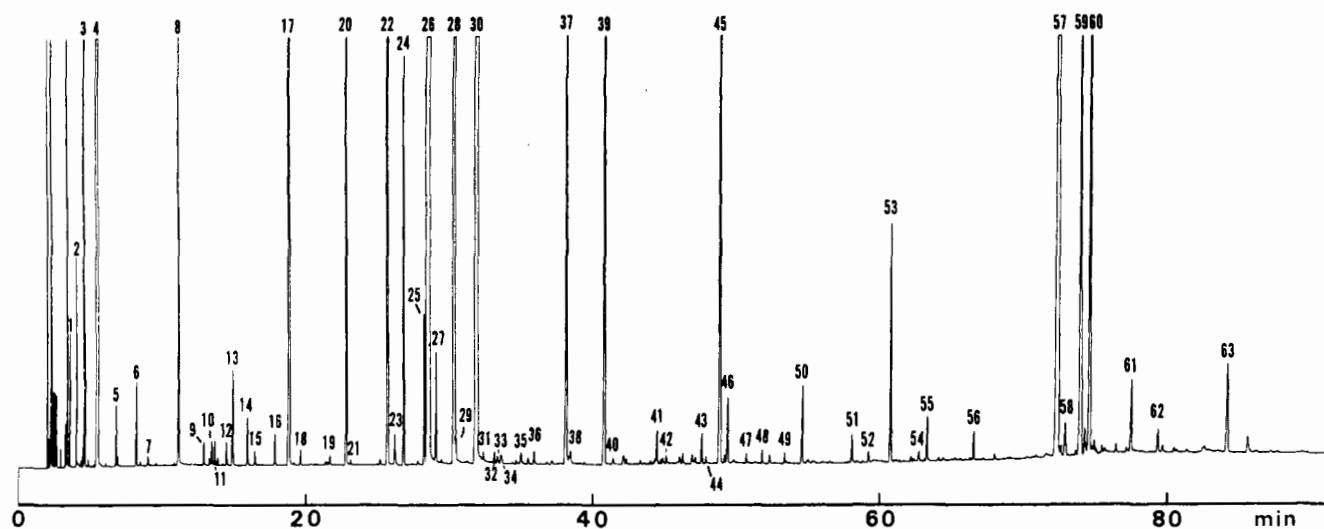
Columns A and B were used to chromatograph nectarine samples prepared by vacuum distillation-extraction while column C was used only to analyze the headspace samples.

**Gas Chromatography-Mass Spectrometry.** A Finnigan MAT 4500 GC/MS/INCOS system (Finnigan MAT, San Jose, CA) equipped with the same capillary columns (columns A and B) as in the GC analyses was used. A flow rate of 1.01 mL/min (30 °C) was used for column A. A split ratio of 1:27 was employed. The column temperature was programmed from 30 to 180 °C at 3 °C/min. For column B the oven temperature was programmed from 30 °C (2-min hold) to 150 °C at 2 °C/min and then to 250 °C at 4 °C/min. A flow rate of 1.21 mL/min (30 °C) was used for column B. For headspace analysis, this unit was fitted with a headspace inlet system operationally identical with that described above. A flow controller maintained the carrier flow through the 60 m × 0.32 mm (i.d.) DB-1 fused silica capillary column (3.9 mL/min at 50 °C). Helium was employed as carrier gas for all three columns. In all cases, the column outlet ends were threaded directly to the ion source of the quadrupole mass spectrometer. The mass spectrometer was repetitively scanned from  $m/z$  33 to 350 in a 1-s cycle. The instrument was operated in the electron impact mode at an ionization voltage of 70 eV.

**Infrared Spectroscopy.** An IBM-32 Fourier transform infrared spectrometer was used. Samples were run neat between two salt (NaCl) plates. The sampling chamber was purged for at least 5 min after the sample was added to remove CO<sub>2</sub> and water vapor. Generally, 40 scans were taken per sample at a resolution of 2 cm<sup>-1</sup>.

**Component Identification.** Sample components were tentatively identified by mass spectrum matching with a mass spectral library collection, using the Finnigan MAT INCOS data system. The reference library is basically the NIH-EPA collection, supplemented by 1400-1500 additional spectra from other collections, and from previous work in our laboratory. In the absence of suitable reference spectra, samples of suspected components were obtained or synthesized and their mass spectra acquired. Tentative MS identifications were verified by comparison of the component's experimental retention index (*I*) with that of an authentic reference standard. The retention index system proposed by Kováts (1958) was utilized.

**Reference Compounds.** Esters were prepared by acid-catalyzed esterification of the corresponding acid and alcohol. (*Z*)-3-Octenoic acid was prepared from 3-octyn-1-ol by a method similar to that described by Stoffel and Ecker (1969). Methyl (*Z*)-3-octenoate had the following spectral properties: mass spectrum,  $m/z$  (relative intensity) 156 (3), 124 (65), 113 (11), 101 (6), 96 (58), 85 (28), 83 (30), 82 (83), 74 (100), 67 (32), 59 (54), 55 (89), 41 (51); <sup>1</sup>H NMR (360 MHz, CDCl<sub>3</sub>)  $\delta$  0.89 (3 H, t, *J* = 6.9 Hz, CH<sub>3</sub>CH<sub>2</sub>), 1.24-1.40 (4 H, m, CH<sub>2</sub>CH<sub>2</sub>), 2.04 (2 H, dt, *J* = 6.6, 8.0 Hz, CH<sub>2</sub>CH=), 3.08 (2 H, d, *J* = 5.8 Hz, CH<sub>2</sub>CO), 3.68 (3 H, s, OCH<sub>3</sub>), 5.49-5.63 (2 H, m, CH=CH); FTIR



**Figure 1.** Capillary gas chromatogram of nectarine volatiles obtained by vacuum distillation with subsequent continuous solvent extraction (trichlorofluoromethane-dichloromethane, 9:1, v/v). Temperature programmed from 30 °C (2 min isothermal) to 180 °C at 2 °C/min on a 60 m × 0.25 mm (i.d.) DB-WAX column (column A). The peak numbers correspond to the numbers in Table I.

spectrum (neat) bands at 1743 (C=O stretch), 1658 (C=C stretch), 700 (C—H out-of-plane bend, cis)  $\text{cm}^{-1}$ . Methyl (*Z*)-4-decenoate possessed the following spectral properties: mass spectrum,  $m/z$  (relative intensity) 184 (3), 152 (29), 141 (2), 135 (8), 123 (13), 110 (59), 96 (35), 84 (35), 74 (100), 69 (42), 55 (49), 41 (46);  $^1\text{H NMR}$  (360 MHz,  $\text{CDCl}_3$ )  $\delta$  0.88 (3 H, t,  $J = 6.8$  Hz,  $\text{CH}_3\text{CH}_2$ ), 1.20–1.40 (6 H, m,  $\text{CH}_2$ ), 2.03 (2 H, dt,  $J = 6.8, 7.2$  Hz,  $\text{CH}_2\text{CH}=\text{CH}$ ), 2.30–2.40 (4 H, overlapping signals,  $=\text{CHCH}_2\text{CH}_2\text{CO}$ ), 3.66 (3 H, s,  $\text{OCH}_3$ ), 5.27–5.37 (1 H, m,  $\text{CH}=\text{CH}$ ), 5.41 (1 H, dt,  $J = 7.2, 10.8$  Hz, cis,  $\text{CH}=\text{CH}$ ); FTIR spectrum (neat) bands at 1745 (C=O stretch), 1656 (C=C stretch), 727 (C—H out-of-plane bend, cis)  $\text{cm}^{-1}$ . Ethyl (*Z*)-4-decenoate had the following spectral properties: mass spectrum,  $m/z$  (relative intensity) 198 (3), 169 (<1), 152 (45), 137 (17), 123 (16), 110 (96), 101 (22), 96 (57), 88 (100), 84 (51), 69 (71), 55 (69), 41 (68);  $^1\text{H NMR}$  (360 MHz,  $\text{CDCl}_3$ )  $\delta$  0.88 (3 H, t,  $J = 6.8$  Hz,  $\text{CH}_3\text{CH}_2$ ), 1.18–1.40 (6 H, m,  $\text{CH}_2$ ), 1.25 (3 H, t,  $J = 7.2$  Hz,  $\text{OCH}_2\text{CH}_3$ ), 2.03 (2 H, dt,  $J = 7.0, 7.3$  Hz,  $\text{CH}_2\text{CH}=\text{CH}$ ), 2.25–2.41 (4 H, m,  $=\text{CHCH}_2\text{CH}_2$ ), 4.12 (2 H, q,  $J = 7.1$  Hz,  $\text{OCH}_2$ ), 5.27–5.36 (1 H, m,  $\text{CH}=\text{CH}$ ), 5.41 (1 H, dt,  $J = 7.0, 10.6$  Hz, cis,  $\text{CH}=\text{CH}$ ); FTIR spectrum (neat) bands at 1740 (C=O stretch), 1653 (C=C stretch), 728 (C—H out-of-plane bend, cis)  $\text{cm}^{-1}$ . 2-Propyl octanoate had the following spectral properties: mass spectrum,  $m/z$  (relative intensity) 145 (66), 144 (37), 127 (91), 115 (8), 102 (54), 101 (23), 84 (24), 73 (32), 60 (79), 57 (56), 43 (100);  $^1\text{H NMR}$  (360 MHz,  $\text{CDCl}_3$ )  $\delta$  0.87 (3 H, t,  $J = 6.7$  Hz,  $\text{CH}_3\text{CH}_2$ ), 1.22 (6 H, d,  $J = 6.3$  Hz,  $(\text{CH}_2)_2\text{CH}$ ), 1.22–1.36 (8 H, m,  $(\text{CH}_2)_4$ ), 1.61 (2 H, m,  $\text{CH}_2\text{CH}_2\text{CO}$ ), 2.24 (2 H, t,  $J = 7.5$  Hz,  $\text{CH}_2\text{CO}$ ), 4.99 (1 H, sept,  $J = 6.3$  Hz,  $\text{CH}(\text{CH}_3)_2$ ). (*Z*)-3-Hexenyl heptanoate had the following spectral properties: mass spectrum,  $m/z$  (relative intensity) 113 (27), 83 (14), 82 (100), 67 (53), 55 (18), 43 (29); FTIR spectrum (neat) bands at 1740 (C=O stretch), 1656 (C=C stretch), and 727 (C—H out-of-plane bend, cis)  $\text{cm}^{-1}$ . (*Z*)-3-Hexenyl octanoate had the following spectral properties: mass spectrum,  $m/z$  (relative intensity) 127 (20), 83 (14), 82 (100), 67 (45), 57 (26), 55 (19), 41 (18); FTIR spectrum (neat) bands at 1740 (C=O stretch), 1656 (C=C stretch), 725 (C—H out-of-plane bend, cis)  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (360 MHz,  $\text{CDCl}_3$ )  $\delta$  0.87 (3 H, t,  $J = 6.7$  Hz,  $\text{CH}_3\text{CH}_2$ ), 0.96 (3 H, t,  $J = 7.5$  Hz,  $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}$ ), 1.20–1.37 (8 H, m,  $(\text{CH}_2)_4$ ), 1.61 (2 H, m,  $\text{CH}_2\text{CH}_2\text{CO}$ ), 2.05 (2 H, dq,  $J = 7.4, 7.5$  Hz,  $=\text{CHCH}_2\text{CH}_3$ ), 2.28 (2 H, t,  $J = 7.5$  Hz,  $\text{CH}_2\text{CO}$ ), 2.36 (2 H, dt,  $J = 6.9, 6.9$  Hz,

$\text{CH}_2\text{CH}=\text{CH}$ ), 4.06 (2 H, t,  $J = 6.9$  Hz,  $\text{OCH}_2$ ), 5.31 (1 H, dt,  $J = 7.3, 10.8$  Hz, cis,  $\text{CH}=\text{CH}$ ), 5.50 (1 H, dt,  $J = 7.3, 10.8$  Hz, cis,  $\text{CH}=\text{CH}$ ).

Other reference standards were obtained from commercial sources or received as gifts.

## RESULTS AND DISCUSSION

The volatile constituents of fresh, tree-ripened nectarines were examined by two different sampling methods. The first method utilized vacuum distillation of blended fruit followed by continuous liquid-liquid extraction while the second method involved dynamic headspace sampling of the intact fruit. Table I lists the nectarine constituents identified in samples prepared by vacuum distillation-extraction. The total amount of volatile material isolated (based on GC peak areas; assuming all response factors = 1) by the vacuum distillation-extraction method was in the range of 4–10 ppm of the fruit pulp and skin. Figure 1 shows a GC/FID chromatogram (column A) of nectarine volatiles isolated by vacuum distillation-extraction. A separate batch of nectarines was prepared by the same vacuum distillation-extraction procedure except this time the skin was excluded and only the pulp sampled. This sample was analyzed on a column of different polarity (DB-1, column B). In general, the resolution of constituents was much better on the polar DB-WAX column. Though the major constituents could be identified on both columns, more constituents were identified on the DB-WAX column. However, there were 11 additional constituents identified with the DB-1 column. This may reflect differences in composition of the two nectarine batches as well as the different selectivity of the DB-WAX and DB-1 columns.

There are both qualitative and quantitative differences in the constituents found by the two different sampling techniques. This reflected differences in the composition of the skin and pulp as well as the enzymatic formation of secondary volatiles caused by disruption of the fruit tissues. The blended pulp was characterized by high levels of  $\text{C}_8$  compounds derived from peroxidation of unsaturated fatty acids (Frankel, 1982; Schreier, 1984). A high level of oxidoreductase activity in the fruit was evidenced by the large amounts of the alcohols hexanol (27.52%), (*E*)-2-hexenol (24.64%), and (*Z*)-3-hexenol (9.97%) compared to the levels of the corresponding aldehydes hexanal

Table I. Volatile Constituents of Nectarine: Vacuum-Distilled Blended Fruit

peak no. <sup>a</sup>	constituent	<i>I</i> <sup>DB-WAX</sup>		area <sup>b</sup>	peak no. <sup>a</sup>	constituent	<i>I</i> <sup>DB-WAX</sup>		area <sup>b</sup>
		exptl	ref				exptl	ref	
1	methyl acetate	825	827	0.09	39	linalool <sup>f</sup>	1551	1551	2.91
2	(1,2-dichloroethene) <sup>c,d</sup>	856			40	1-octanol	1562	1562	tr
3	ethyl acetate	891	888	2.51	41	hotrienol	1610	1611	0.05
4	dichloromethane <sup>c</sup>	928	925		42	methyl (Z)-4-decenoate <sup>e</sup>	1621	1622	0.01
5	propyl acetate <sup>e,f</sup>	976	976	0.06	43	1-nonanol <sup>e,f</sup>	1664	1664	0.05
6	2-methylpropyl acetate <sup>e,f</sup>	1014	1014	0.09	44	(E)-2-hexenyl hexanoate <sup>e</sup>	1668	1668	tr
7	toluene <sup>e,f</sup>	1035	1035	0.01	45	γ-hexalactone <sup>f</sup>	1684	1683	1.40
8	hexanal <sup>f</sup>	1079	1079	0.91	46	α-terpineol <sup>f</sup>	1692	1693	0.11
9	3-pentanol <sup>e,f</sup>	1112	1112	0.03	47	(E)-2-nonenol <sup>e</sup>	1715	1716	0.02
10	3-methylbutyl acetate	1122	1122	0.04	48	trans-pyran linalool oxide <sup>e</sup>	1736	1736	0.02
11	4-methyl-3-penten-2-one <sup>e</sup>	1127	1127	0.03	49	cis-pyran linalool oxide <sup>e</sup>	1763	1764	0.02
12	(Z)-3-hexenal <sup>e</sup>	1142	1142	0.03	50	γ-heptalactone <sup>f</sup>	1784	1785	0.13
13	(3-methyl-4-pentenal) <sup>d</sup>	1148		0.13	51	geraniol <sup>f</sup>	1849	1850	0.05
14	1-penten-3-ol <sup>e</sup>	1165	1165	0.06	52	benzyl alcohol	1870	1872	0.02
15	pentyl acetate <sup>f</sup>	1174	1174	0.02	53	γ-octalactone <sup>f</sup>	1897	1898	0.41
16	((Z)-2-hexenal) <sup>d,e</sup>	1193		0.05	54	benzothiazole <sup>e,f</sup>	1936	1937	0.02
17	(E)-2-hexenal <sup>f</sup>	1209	1209	4.70	55	δ-octalactone <sup>e,f</sup>	1948	1949	0.08
18	unknown	1222		0.02	56	γ-nonalactone <sup>f</sup>	2011	2012	0.05
19	1-pentanol	1256	1256	0.01	57	γ-decalactone <sup>f</sup>	2131	2129	9.85
20	hexyl acetate <sup>f</sup>	1272	1272	1.32	58	unknown	2142		0.08
21	acetoin <sup>e</sup>	1277	1278	tr	59	6-pentyl-α-pyrone <sup>f</sup>	2163	2164	1.31
22	(Z)-3-hexenyl acetate <sup>f</sup>	1315	1315	3.77	60	δ-decalactone <sup>f</sup>	2178	2178	2.24
23	(Z)-2-pentenol <sup>e</sup>	1323	1324	0.05	61	(Z)-dec-7-en-5-olide <sup>e,f</sup>	2236	2239	0.14
24	(E)-2-hexenyl acetate <sup>f</sup>	1333	1333	0.63		[jasmine lactone]			
25	unknown	1355		0.23	62	unknown	2273		0.05
26	1-hexanol <sup>f</sup>	1361	1358	27.52	63	γ-dodecalactone <sup>f</sup>	2354	2355	0.23
27	(E)-3-hexenol <sup>e,f</sup>	1367	1367	0.15		3-methyl-1-butanol <sup>g</sup>	(724) <sup>h</sup>	(725) <sup>h</sup>	
28	(Z)-3-hexenol <sup>f</sup>	1386	1385	9.97		ethyl 2-methylpropanoate <sup>e,g</sup>	(751)	(750)	
29	methyl octanoate <sup>e</sup>	1387	1387	0.03		2-hexanone <sup>e,g</sup>	(769)	(769)	
30	(E)-2-hexenol <sup>f</sup>	1410	1408	24.64		butyl acetate <sup>g</sup>	(800)	(800)	
31	(Z)-2-hexenol <sup>e</sup>	1417	1418	0.01		6-methyl-5-hepten-2-one <sup>e,g</sup>	(966)	(966)	
32	unknown	1430		0.02		2-ethylhexanol <sup>e,g</sup>	(1018)	(1018)	
33	ethyl octanoate	1434	1434	0.01		acetophenone <sup>e,g</sup>	(1026)	(1027)	
34	trans-furan linalool oxide <sup>e</sup>	1438	1439	0.02		4-terpineol <sup>g</sup>	(1153)	(1153)	
35	1-heptanol <sup>e,f</sup>	1460	1460	0.02		geranylacetone <sup>e,g</sup>	(1426)	(1426)	
36	unknown	1474		0.02		tetradecanoic acid <sup>e,g</sup>	(1749)	(1750)	
37	benzaldehyde <sup>f</sup>	1507	1507	2.33		hexadecanoic acid <sup>e,g</sup>	(1943)	(1944)	
38	unknown	1513		0.02					

<sup>a</sup>The peak numbers correspond to the numbers in Figure 1. <sup>b</sup>Peak area percentage of total FID area excluding the solvent peaks (assuming all response factors of 1). tr represents less than 0.01%. <sup>c</sup>Solvent or solvent contaminant. <sup>d</sup>Tentative or partial identifications enclosed in parentheses. <sup>e</sup>Not previously reported in peach. <sup>f</sup>Identity additionally confirmed by GC-MS and retention index on a 30 m × 0.25 mm (i.d.) DB-1 column (column B). <sup>g</sup>Compounds identified by retention index and mass spectrum obtained on DB-1 column (column B) not detected in DB-WAX run. <sup>h</sup>Retention indices in parentheses were obtained on DB-1 column (column B).

(0.91%), (E)-2-hexenal (4.70%), and (Z)-3-hexenal (0.03%).

The esters detected in the blended pulp and skin consisted mainly of acetates. The major esters found were (Z)-3-hexenyl acetate (3.77%), ethyl acetate (2.51%), hexyl acetate (1.32%), and (E)-2-hexenyl acetate (0.63%).

Numerous lactones were identified in the blended pulp and skin. The major lactones include γ-decalactone (9.85%), δ-decalactone (2.24%), γ-hexalactone (1.40%), and γ-octalactone (0.41%). Despite these high levels, only a small amount of γ-hexalactone (tentatively identified, 0.07%) and a trace of γ-octalactone were detected with the dynamic headspace sampling method. This was somewhat surprising since Ismail et al. (1981a) found higher percentages of γ-nonalactone and γ-decalactone in the headspace of intact plums. This difference may be due to their longer sampling period compared to that used in our study (12 vs 0.5 h). δ-Octalactone and (Z)-dec-7-en-5-olide (jasmine lactone) were not previously reported in peach. Jasmine lactone has been previously found in jasmine absolute (Winter et al., 1962), tea (Yamanishi et al., 1973; Cazenave and Horman, 1974), gardenia flower absolute (Hattori et al., 1978), and Alphonso mango (Idstein and Schreier, 1985).

Another major constituent identified was 6-pentyl-α-pyrone (1.31%). This compound had been previously reported in peach (Sevenants and Jennings, 1971). The

compound has been synthesized by Nobuhara (1969) who reported its odor as butter or butter cake and Pittet and Klaiber (1975) who described its odor as coconut, peach-like, lactonic, and green. This compound has been shown to be the predominant volatile of the fungus *Trichoderma viride* (Collins and Halim, 1972).

Other major volatile constituents include benzaldehyde (2.33%) and linalool (2.91%). Benzaldehyde was only detected at trace levels in the headspace of the intact fruit; linalool was found at reduced levels in the headspace as well as in the samples prepared by direct extraction (Engel et al., 1988), suggesting these compounds are present in both free and bound forms. Enzymatic activity as a result of tissue disruption, i.e. blending of the pulp during sample preparation, releases these constituents from their bound state in a manner similar to that reported in papaya fruit pulp (Heidlas et al., 1984).

Geranylacetone and 6-methylhept-5-en-2-one can be regarded as norterpeneoids arising from isoprenoid degradation (Buttery et al., 1969; Buttery 1981; Enzell et al., 1977).

Tetradecanoic and hexadecanoic acid were found in the extract. Free carboxylic acids are only slightly soluble in the nonpolar DB-1 phase and hence readily yield overloaded peaks (Yabumoto et al., 1980). Their retention behavior is variable and is strongly dependent on the amount chromatographed on the column. To minimize

Table II. Headspace Constituents of Intact, Tree-Ripened Nectarine

peak no. <sup>a</sup>	constituent	<i>I</i> <sup>DB-1</sup>		% area <sup>b</sup>	peak no. <sup>a</sup>	constituent	<i>I</i> <sup>DB-1</sup>		% area <sup>b</sup>
		exptl	ref				exptl	ref	
1	(dichlorodifluoromethane) <sup>c,f</sup>			tr <sup>d</sup>	60	4-ethylmethylbenzene <sup>f</sup>	940	946	tr
2	(acetaldehyde) <sup>c</sup>		400	0.47	61	2-ethylmethylbenzene <sup>f</sup>	955	961	tr
3	(ethanol) <sup>c</sup>		440	57.44	62	(2,6,6-trimethyl-2-ethenyltetrahydropyran) <sup>c,f</sup>	957		tr
4	(acetone) <sup>c,f</sup>		468						
5	(2-propanol) <sup>c,f</sup>		475	1.04	63	3-octanone <sup>f</sup>	962	964	tr
6	methyl acetate	(508) <sup>e</sup>	508	7.21	64	(monoterpene) <sup>c</sup>	966		0.01
7	2-methylpentane <sup>f</sup>	556	560	0.06	65	1,2,4-trimethylbenzene <sup>f</sup>	971	978	tr
8	2,3-butanedione <sup>f</sup>	563	558	0.12	66	2-pentylfuran <sup>f</sup>	975	977	0.01
9	2-butanone <sup>f</sup>	567	568	0.03	67	myrcene <sup>f</sup>	980	981	0.51
10	3-methylpentane <sup>f</sup>	571	576	0.04	68	ethyl hexanoate	981	981	0.12
11	2-methylfuran <sup>f</sup>	585	589	tr	69	( <i>Z</i> )-3-hexenyl acetate	987	986	1.89
12	(3-methylfuran) <sup>c,f</sup>	600		tr	70	hexyl acetate	(995)	995	0.25
13	ethyl acetate	(600)	600	22.38	71	decane <sup>f</sup>	998	1000	0.01
14	chloroform <sup>f</sup>	606	601	tr	72	$\alpha$ -terpinene <sup>f</sup>	1001	1008	0.01
15	(C <sub>8</sub> H <sub>12</sub> hydrocarbon) <sup>c</sup>	615		0.06	73	<i>p</i> -cymene <sup>f</sup>	1004	1011	0.05
16	2-methylpropanol <sup>f</sup>	617	608	0.06	74	methyl heptanoate <sup>f</sup>	1005	1006	0.03
17	1,1,1-trichloroethane <sup>f</sup>	621	629	tr	75	$\beta$ -phellandrene <sup>f</sup>	1011	1018	0.05
18	(C <sub>8</sub> H <sub>10</sub> hydrocarbon) <sup>c</sup>	625		0.02	76	limonene	1014	1020	0.25
19	benzene <sup>f</sup>	634	644	0.01	77	( <i>Z</i> )- $\beta$ -ocimene <sup>f</sup>	1025	1026	0.19
20	(C <sub>8</sub> H <sub>12</sub> hydrocarbon) <sup>c</sup>	641		tr	78	( $\gamma$ -hexalactone) <sup>c</sup>	1032	1003	0.07
21	2-propyl acetate <sup>f</sup>	644	638	tr	79	( <i>E</i> )- $\beta$ -ocimene <sup>f</sup>	1036	1037	0.26
22	1-penten-3-ol <sup>f</sup>	663	658	0.11	80	$\gamma$ -terpinene <sup>f</sup>	1043	1048	0.02
23	3-pentanone <sup>f</sup>	666	669	0.03	81	(dimethylstyrene) <sup>c,f</sup>	1067		0.02
24	trichloroethylene <sup>f</sup>	672	686	tr	82	terpinolene <sup>f</sup>	1073	1077	0.06
25	3-pentanol <sup>f</sup>	680	678	0.14	83	ethyl heptanoate <sup>f</sup>	1081	1080	0.03
26	heptane <sup>f</sup>	691	700	tr	84	linalool	1082	1083	0.34
27	ethyl propanoate <sup>f</sup>	693	692	tr	85	methyl ( <i>Z</i> )-3-octenoate <sup>f</sup>	1095	1103	0.05
28	propyl acetate <sup>f</sup>	(695)	695	0.16	86	methyl octanoate <sup>f</sup>	1106	1106	1.08
29	methyl butanoate <sup>f</sup>	702	704	0.02	87	naphthalene <sup>f</sup>	1146	1157	0.01
30	(C <sub>7</sub> H <sub>14</sub> hydrocarbon) <sup>c</sup>	705		tr	88	$\alpha$ -terpineol	1166	1170	0.03
31	3-methylbutanol	720	714	0.02	89	( <i>Z</i> )-3-hexenyl butanoate <sup>f</sup>	1166	1168	0.03
32	2-methylbutanol <sup>f</sup>	724	718	tr	90	ethyl ( <i>E</i> )-4-octenoate <sup>f</sup>	1169	1169	0.06
33	toluene <sup>f</sup>	739	748	0.02	91	hexyl butanoate <sup>f</sup>	1174	1175	tr
34	ethyl 2-methylpropanoate <sup>f</sup>	742	738	tr	92	ethyl octanoate	1179	1180	1.84
35	2-methylpropyl acetate <sup>f</sup>	755	750	0.27	93	octyl acetate <sup>f</sup>	(1193)	1193	tr
36	methyl 3-methylbutanoate	758	754	0.03	94	$\gamma$ -octalactone	1209	1210	tr
37	hexanal	769	772	0.01	95	( <i>Z</i> )-3-hexenyl 3-methylbutanoate <sup>f</sup>	1217	1218	0.11
38	ethyl butanoate <sup>f</sup>	783	780	0.05	96	2-propyl octanoate <sup>f</sup>	1218	1218	tr
39	tetrachloroethylene <sup>f</sup>	785	800	tr	97	ethyl ( <i>E</i> )-2-octenoate <sup>f</sup>	1223	1223	tr
40	octane <sup>f</sup>	795	800	tr	98	hexyl 3-methylbutanoate <sup>f</sup>	1225	1225	0.02
41	butyl acetate	(796)	796	0.01	99	2-methylnaphthalene <sup>f</sup>	1257	1268	tr
42	( <i>Z</i> )-3-hexenol	836	834	0.21	100	1-methylnaphthalene <sup>f</sup>	1271	1282	tr
43	<i>m</i> -xylene <sup>f</sup>	845	852	0.02	101	ethyl nonanoate <sup>f</sup>	1279	1279	tr
44	<i>p</i> -xylene <sup>f</sup>	846	853	tr	102	methyl ( <i>Z</i> )-4-decenoate <sup>f</sup>	1288	1289	0.10
45	( <i>E</i> )-2-hexenol	850	844	tr	103	tridecane <sup>f</sup>	1299	1300	0.01
46	hexanol	854	847	0.02	104	methyl decanoate <sup>f</sup>	1306	1307	tr
47	3-methylbutyl acetate	858	855	0.19	105	(methyl(?) 3-decenoate) <sup>c</sup>	1321		0.08
48	2-methylbutyl acetate <sup>f</sup>	861	858	0.01	106	ethyl ( <i>Z</i> )-4-decenoate <sup>f</sup>	1359	1361	0.10
49	styrene	862	871	tr	107	( <i>Z</i> )-3-hexenyl hexanoate <sup>f</sup>	1360	1360	0.06
50	3-methyl-3-butenyl acetate <sup>f</sup>	864	862	0.01	108	hexyl hexanoate <sup>f</sup>	1367	1369	0.01
51	<i>o</i> -xylene <sup>f</sup>	866	876	tr	109	ethyl decanoate <sup>f</sup>	1377	1379	tr
52	pentyl acetate	(895)	895	0.05	110	(ethyl(?) 3-decenoate) <sup>c</sup>	1391		0.03
53	3-methyl-2-butenyl acetate <sup>f</sup>	901	902	tr	111	tetradecane <sup>f</sup>	1397	1400	tr
54	methyl hexanoate <sup>f</sup>	905	906	0.08	112	( <i>Z</i> )-3-hexenyl heptanoate <sup>f</sup>	1459	1460	tr
55	methyl ( <i>E</i> )-3-hexenoate <sup>f</sup>	910	913	tr	113	pentadecane <sup>f</sup>	(1500)	1500	0.28
56	benzaldehyde	917	926	tr	114	( <i>Z</i> )-3-hexenyl octanoate <sup>f</sup>	1559	1559	0.07
57	(monoterpene) <sup>c</sup>	920		tr	115	hexadecane <sup>f</sup>	(1600)	1600	tr
58	$\alpha$ -pinene <sup>f</sup>	931	929	tr	116	heptadecane	(1700)	1700	0.12
59	3-ethylmethylbenzene <sup>f</sup>	939	945	tr					

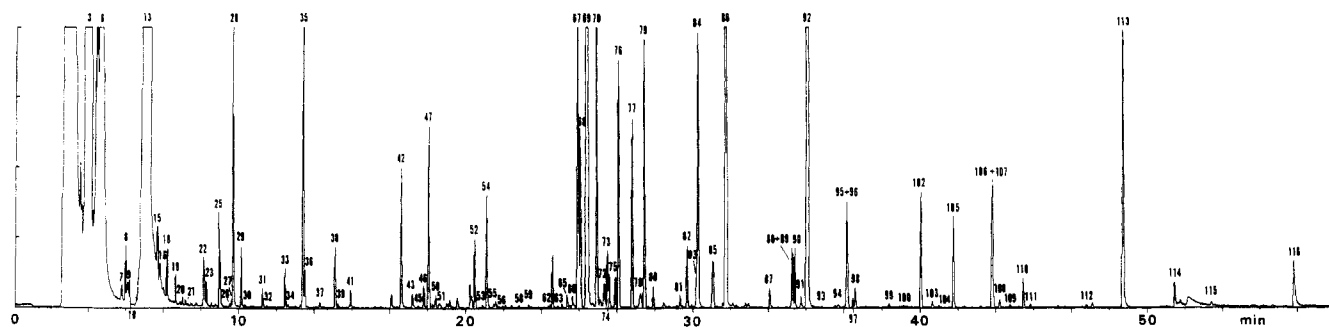
<sup>a</sup>The peak numbers correspond to the numbers in Figure 2. <sup>b</sup>Uncorrected area percent values from HP 5830 integration of FID signal. <sup>c</sup>Tentative or partial identifications enclosed in parentheses. <sup>d</sup>tr = less than 0.005%. <sup>e</sup>Reference *I* values taken as markers for experimental *I* scale enclosed in parentheses. <sup>f</sup>Not previously reported in peach.

this effect, care was taken to chromatograph similar amounts of reference standard acids as were present in the extract.

Components identified in the intact ripe nectarine headspace sample are listed in Table II. A reconstructed ion chromatogram from GC-MS analysis of nectarine headspace is shown in Figure 2. In a number of instances tentative MS-based identifications could not be verified, either because an authentic sample of the compound in question was not available or because the experimental *I*

value could not be calculated, notably at the start of the headspace chromatographic run. Such identifications are considered tentative and are enclosed in parentheses in Table II, as are the names of several compounds only partially characterized from mass spectral data. Although not supported by *I* matching, identifications of components at the front of the chromatogram are valid, if only because so few structural possibilities exist for these compounds.

Two factors complicate the use of *I* values in headspace gas chromatographic runs such as these. First, consider-



**Figure 2.** Reconstructed ion chromatogram from GC-MS analysis of nectarine headspace volatiles. Temperature programmed from 0 to 225 °C at 3 °C/min on a 60 m × 0.32 mm (i.d.) DB-1 column. The peak numbers correspond to the numbers in Table II.

able water vapor is introduced into the methyl silicone capillary column along with the headspace sample components; this has an effect upon the retention behavior of the sample components, retarding the elution of the more polar constituents relative to the nonpolar ones. Since the *I* scale employed is based upon the elution behavior of the nonpolar normal hydrocarbon series, the net effect is that moderate to very polar compounds exhibit higher experimental *I* values than would be found in the absence of water. Second, cointroduction of the normal hydrocarbon reference series with experimental sample is usually required to permit calculation of experimental *I* values. This is not readily accomplished with trapped headspace samples. These problems were accommodated with fair success in the present study by using a series of aliphatic acetates (along with their *n*-hydrocarbon-based *I* values) as markers in the nectarine headspace GC-MS run, supplemented by the 15- through 17-carbon normal hydrocarbons present in the nectarine sample. Members of several homologous saturated normal aliphatic ester series were readily identified from their mass spectra and elution sequence. Since a linear temperature program was used, members of these series eluted in a fairly regular manner. The series from methyl through decyl acetate and the normal C<sub>16</sub> hydrocarbon were required to bracket nearly all of the headspace components. Heptyl, nonyl, and decyl acetates could not be found in the headspace samples, but when a plot of *I* vs elution time was prepared for the acetate series, as well as for the methyl and ethyl ester series, expected elution times for the three remaining acetates were obtained. By using this secondary aliphatic acetate scale the disruptive effects of water vapor are reduced, for most of the identified headspace components are of similar or greater polarity.

Most of the experimental *I* values are within a few units of the corresponding reference *I* values determined with an authentic sample. This is particularly true with the various carboxylic esters, as might be expected. The aromatic and aliphatic hydrocarbons all exhibit experimental *I* values 2-11 units lower than their reference values. In contrast, the few primary alcohols present have experimental *I* values 6 units larger than their reference values. The only major discrepancy between mass spectral data and experimental *I* appears with a peak at 1661 s. MS data indicate  $\gamma$ -hexalactone, but the reference and experimental *I* values differ by 29 units. Because this lactone is found in nectarines, it is included in Table II but must be considered only tentatively identified.

Quantitatively, the bulk of the headspace sample consisted of ethanol, ethyl acetate, and methyl acetate. These compounds were accompanied by a diverse assortment of aliphatic esters, monoterpenoids, alcohols, aliphatic and aromatic hydrocarbons, and halogenated compounds. The halogenated compounds, such as dichlorodifluoromethane,

are presumably contaminants, having been found in headspace blanks and in headspace GC-MS examinations of numerous other sample substrates. A number of the aromatic hydrocarbons, including benzene, toluene, the xylenes, and 1,2,4-trimethylbenzene, also are found on occasion at trace levels in blank headspace runs. The presence of a variety of monoterpene hydrocarbons is noteworthy. None were identified in the vacuum distillation extract though Engel et al. (1988) found a number of them using direct solvent extraction.

A variety of saturated and unsaturated esters were identified in the headspace sample. Methyl octanoate (1.08%) and ethyl octanoate (1.84%) were major constituents found in the headspace. Both methyl and ethyl (*Z*)-4-decenoate were found in the headspace of intact fruit, but only methyl (*Z*)-4-decenoate was detected in the sample prepared by vacuum distillation-extraction. Similarly, in their studies of plum volatiles, Ismail et al. (1981a,b) found ethyl (*Z*)-4-decenoate in the headspace of intact fruit but failed to detect the ester in the corresponding juice sample prepared by vacuum distillation-extraction. This may reflect differences in concentration of volatiles in the skin and pulp in an analogous manner as found in grapes (Bayonove et al., 1974). Methyl (*Z*)-4-decenoate has been previously identified as an important hop oil constituent (Guadagni et al., 1966) while ethyl (*Z*)-4-decenoate has been found in plum (Ismail et al., 1981a,b), quince fruit (Tsuneya et al., 1983), quince peel (Umano et al., 1986), and Red Delicious apples (Berger et al., 1984). Both the methyl and ethyl esters of (*Z*)-4-decenoic acid have been reported in Barlett pear (Heinz and Jennings, 1966) and pineapple (Näf-Müller and Willhalm, 1971). The formation of methyl and ethyl (*Z*)-4-decenoate through  $\beta$ -oxidation of linoleic acid has been discussed by Jennings and Tressl (1974). The presence of methyl (*Z*)-3-octenoate is interesting since this ester has not been previously identified in food (van Straten and Maarse, 1983). There were also a number of (*Z*)-3-hexenyl esters present in the headspace.

#### ACKNOWLEDGMENT

We thank Jeff deRopp for recording the NMR spectra and T. R. Mon for providing the reference *I* values and assisting with the headspace runs.

**Registry No.** Dichlorodifluoromethane, 75-71-8; acetaldehyde, 75-07-0; ethanol, 64-17-5; acetone, 67-64-1; 2-propanol, 67-63-0; methyl acetate, 79-20-9; 2-methylpentane, 107-83-5; 2,3-butanedione, 431-03-8; 2-butanone, 78-93-3; 3-methylpentane, 96-14-0; 2-methylfuran, 534-22-5; 3-methylfuran, 930-27-8; ethyl acetate, 141-78-6; chloroform, 67-66-3; 2-methylpropanol, 78-83-1; 1,1,1-trichloroethane, 71-55-6; benzene, 71-43-2; 2-propyl acetate, 108-21-4; 1-penten-3-ol, 616-25-1; 3-pentanone, 96-22-0; trichloroethylene, 79-01-6; 3-pentanol, 584-02-1; heptane, 142-82-5; ethyl propanoate, 105-37-3; propyl acetate, 109-60-4; methyl butanoate, 623-42-7; 3-methylbutanol, 123-51-3; 2-methylbutanol,

137-32-6; toluene, 108-88-3; ethyl 2-methylpropanoate, 97-62-1; 2-methylpropyl acetate, 110-19-0; methyl 3-methylbutanoate, 556-24-1; hexanal, 66-25-1; ethyl butanoate, 105-54-4; tetrachloroethylene, 127-18-4; octane, 111-65-9; butyl acetate, 123-86-4; (*Z*)-3-hexenol, 928-96-1; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; (*E*)-2-hexenol, 928-95-0; hexanol, 111-27-3; 3-methylbutyl acetate, 123-92-2; 2-methylbutyl acetate, 624-41-9; styrene, 100-42-5; 3-methyl-3-butenyl acetate, 5205-07-2; *o*-xylene, 95-47-6; pentyl acetate, 628-63-7; 3-methyl-2-butenyl acetate, 1191-16-8; methyl hexanoate, 106-70-7; methyl (*E*)-3-hexenoate, 13894-61-6; benzaldehyde, 100-52-7;  $\alpha$ -pinene, 80-56-8; 3-(ethylmethyl)benzene, 620-14-4; 4-(ethylmethyl)benzene, 622-96-8; 2,6,6-trimethyl-2-ethenyltetrahydropyran, 7392-19-0; 3-octanone, 106-68-3; 1,2,4-trimethylbenzene, 95-63-6; 2-pentylfuran, 3777-69-3; myrcene, 123-35-3; ethyl hexanoate, 123-66-0; (*Z*)-3-hexenyl acetate, 3681-71-8; hexyl acetate, 142-92-7; decane, 124-18-5;  $\alpha$ -terpinene, 99-86-5; *p*-cymene, 99-87-6; methyl heptanoate, 106-73-0;  $\beta$ -phellandrene, 555-10-2; limonene, 138-86-3; (*Z*)- $\beta$ -ocimene, 3338-55-4;  $\gamma$ -hexalactone, 695-06-7; (*E*)- $\beta$ -ocimene, 3779-61-1;  $\gamma$ -terpinene, 99-85-4; dimethylstyrene, 27576-03-0; terpinolene, 586-62-9; ethyl heptanoate, 106-30-9; linalool, 78-70-6; methyl (*Z*)-3-octenoate, 69668-85-5; methyl octanoate, 111-11-5; naphthalene, 91-20-3;  $\alpha$ -terpineol, 98-55-5; (*Z*)-3-hexenyl butanoate, 16491-36-4; ethyl (*E*)-4-octenoate, 78989-37-4; hexyl butanoate, 2639-63-6; ethyl octanoate, 106-32-1; octyl acetate, 103-09-3;  $\gamma$ -octalactone, 104-50-7; (*Z*)-3-hexenyl 3-methylbutanoate, 35154-45-1; 2-propyl octanoate, 5458-59-3; ethyl (*E*)-2-octenoate, 7367-82-0; hexyl 3-methylbutanoate, 10032-13-0; 2-methylnaphthalene, 91-57-6; 1-methylnaphthalene, 90-12-0; ethyl nonanoate, 123-29-5; methyl (*Z*)-4-decenoate, 7367-83-1; tridecane, 629-50-5; methyl decanoate, 110-42-9; ethyl (*Z*)-4-decenoate, 7367-84-2; (*Z*)-3-hexenyl hexanoate, 31501-11-8; hexyl hexanoate, 6378-65-0; ethyl decanoate, 110-38-3; tetradecane, 61444-41-5; (*Z*)-3-hexenyl heptanoate, 629-59-4; pentadecane, 61444-39-1; (*Z*)-3-hexenyl octanoate, 629-62-9; hexadecane, 544-76-3; heptadecane, 629-78-7; 1,2-dichloroethene, 107-06-2; dichloromethane, 75-09-2; 4-methyl-3-penten-2-one, 141-79-7; (*Z*)-3-hexenal, 6789-80-6; 3-methyl-4-pentenal, 1777-33-9; (*Z*)-2-hexenal, 16635-54-4; (*E*)-2-hexenal, 6728-26-3; 1-pentanol, 71-41-0; acetoin, 513-86-0; (*Z*)-2-pentenol, 1576-95-0; (*E*)-2-hexenyl acetate, 2497-18-9; (*E*)-3-hexenol, 928-97-2; (*Z*)-2-hexenol, 928-94-9; *trans*-furan linalool oxide, 34995-77-2; 1-heptanol, 111-70-6; 1-octanol, 111-87-5; hotrienol, 20053-88-7; methyl (*Z*)-4-decenoate, 7367-83-1; 1-nonanol, 143-08-8; (*E*)-2-hexenyl hexanoate, 53398-86-0; (*E*)-2-nonenol, 31502-14-4; *trans*-pyran linalool oxide, 39028-58-5; *cis*-pyran linalool oxide, 14009-71-3;  $\gamma$ -heptalactone, 105-21-5; geraniol, 106-24-1; benzyl alcohol, 100-51-6; benzothiazole, 95-16-9;  $\delta$ -octalactone, 698-76-0;  $\gamma$ -nonalactone, 104-61-0;  $\gamma$ -decalactone, 706-14-9; 6-pentyl- $\alpha$ -pyrone, 27593-23-3;  $\delta$ -decalactone, 705-86-2; (*Z*)-dec-7-en-5-olide, 25524-95-2;  $\gamma$ -dodecalactone, 2305-05-7; 3-methyl-1-butanol, 123-51-3; 2-hexanone, 591-78-6; 6-methyl-5-hepten-2-one, 110-93-0; 2-ethylhexanol, 104-76-7; acetophenone, 98-86-2; 4-terpineol, 562-74-3; geranylacetone, 3796-70-1; tetradecanoic acid, 544-63-8; hexadecanoic acid, 57-10-3; (*Z*)-3-octenoic acid, 5169-51-7; 2-(ethylmethyl)benzene, 611-14-3.

## LITERATURE CITED

- Bayonove, C.; Cordonnier, R.; Ratier, R. "Localisation de l'Arôme dans la Baie de Raisin: Variétés Muscat d'Alexandrie et Cabernet Sauvignon". *C.R. Seances Acad. Agric. Fr.* 1974, 1321-1328.
- Berger, R. G.; Drawert, F.; Schraufstetter, B. "Über das Natürliche Vorkommen der Ethylester von Octen-, Decen- und Decadiensäure in Äpfeln der Sorte Red Delicious". *Z. Lebensm. Unters. Forsch.* 1984, 178, 104-105.
- Brooks, R. M.; Olmo, H. P. In *Register of New Fruit and Nut Varieties*, 2nd ed.; University of California: Berkeley, 1972; pp 295-320.
- Buttery, R. G. "Vegetable and Fruit Flavors". In *Flavor Research Recent Advances*; Teranishi, R., Flath, R. A., Sugisawa, H., Eds.; Marcel Dekker: New York, Basel, 1981; pp 175-216.
- Buttery, R. G.; Seifert, R. M.; Ling, L. C. "Volatile Tomato Components: Characterization of 6,10,14-Trimethylpentadec-5,9,13-trien-2-one". *Chem. Ind. (London)* 1969, 238.
- Cazenave, P.; Horman, I. "Sur la Composition de l'Arôme de thé Noir V". *Helv. Chim. Acta* 1974, 57, 209-211.
- Collins, R. P.; Halim, A. F. "Characterization of the Major Aroma Constituent of the Fungus *Trichoderma viride* (Pers.)". *J. Agric. Food Chem.* 1972, 20, 437-438.
- Engel, K.-H.; Tressl, R. "Formation of Aroma Components from Nonvolatile Precursors in Passion Fruit". *J. Agric. Food Chem.* 1983, 31, 998-1002.
- Engel, K.-H.; Flath, R. A.; Buttery, R. G.; Mon, T. R.; Ramming, D. W.; Teranishi, R. "Investigation of Volatile Constituents in Nectarines. 1. Analytical and Sensory Characterization of Aroma Components in Some Nectarine Cultivars". *J. Agric. Food Chem.* 1988, preceding paper in this issue.
- Enzell, C. R.; Wahlberg, I.; Aasen, A. J. "Isoprenoids and Alkaloids of Tobacco". In *Progress in the Chemistry of Organic Natural Products*; Herz, W., Grisebach, H., Kirby, G. W., Eds.; Springer-Verlag: New York, 1977; Vol. 34, pp 1-66.
- Flath, R. A.; Ohinata, K. "Volatile Components of the Orchid *Dendrobium Superbum* Rchb.f.". *J. Agric. Food Chem.* 1982, 30, 841-842.
- Frankel, E. N. "Volatile Lipid Oxidation Products". *Prog. Lipid Res.* 1982, 22, 1-33.
- Guadagni, D. G.; Buttery, R. G.; Harris, J. "Odour Intensities of Hop Oil Components". *J. Sci. Food Agric.* 1966, 17, 142-144.
- Hattori, R.; Muraki, S.; Yoshida, T. "Chemical Composition of the Absolute from Gardenia Flower". *Agric. Biol. Chem.* 1978, 42, 1351-1356.
- Heidlas, J.; Lehr, M.; Idstein, H.; Schreier, P. "Free and Bound Terpene Compounds in Papaya (*Carica papaya*, L.) Fruit Pulp". *J. Agric. Food Chem.* 1984, 32, 1020-1021.
- Heinz, D. E.; Jennings, W. G. "Volatile Components of Bartlett Pear V." *J. Food Sci.* 1966, 31, 69-80.
- Idstein, H.; Schreier, P. "Volatile Constituents of Alphonso Mango (*Mangifera indica*)". *Phytochemistry* 1985, 24, 2313-2316.
- Ismail, H. M. M.; Williams, A. A.; Tucknott, O. G. "The Flavour Components of Plums: an Examination of the Aroma Components Present in the Headspace above Four Cultivars of Intact Plums, Marjorie's Seedling, Merton Gem, NA10 and Victoria". *J. Sci. Food Agric.* 1981a, 32, 498-502.
- Ismail, H. M. M.; Williams, A. A.; Tucknott, O. G. "The Flavour of Plums (*Prunus domestica* L.). An Examination of the Aroma Components of Plum Juice from the Cultivar Victoria". *J. Sci. Food Agric.* 1981b, 32, 613-619.
- Jennings, W. G.; Tressl, R. "Production of Volatile Compounds in the Ripening Bartlett Pear". *Chem. Mikrobiol. Technol. Lebensm.* 1974, 3, 52-55.
- Kováts, E. "Gas-Chromatographische Charakterisierung Organischer Verbindungen Teil 1: Retentionsindices Aliphatischer Halogenide, Alkohole, Aldehyde und Ketone". *Helv. Chim. Acta* 1958 41, 1915-1932.
- LaRue, J. H.; Gerdtts, M. "Growing Shipping Peaches and Nectarines in California". Cooperative Extension, University of California Leaflet 2851, 1983.
- Lim, L.; Romani, R. J. "Volatiles and the Harvest Maturity of Peaches and Nectarines". *J. Food Sci.* 1964, 29, 246-253.
- Näf-Müller, R.; Willhalm, B. "Über die Flüchtigen Anteile der Ananas". *Helv. Chim. Acta* 1971, 54, 1880-1890.
- Nobuhara, A. "Syntheses of Unsaturated Lactones. Part III. Flavorous Nature of Some  $\delta$ -Lactones Having the Double Bond at Various Sites". *Agric. Biol. Chem.* 1969, 33, 1264-1269.
- Pittet, A. O.; Klaiber, E. M. "Synthesis and Flavor Properties of Some Alkyl-Substituted  $\alpha$ -Pyrone Derivatives". *J. Agric. Food Chem.* 1975, 23, 1189-1195.
- Schreier, P. In *Chromatographic Studies of Biogenesis of Plant Volatiles*; Huethig Verlag: Heidelberg, West Germany, 1984; pp 33-36.
- Sevenants, M. R.; Jennings, W. G. "Occurrence of 6-Pentyl- $\alpha$ -pyrone in Peach Essence". *J. Food Sci.* 1971, 36, 536.
- Stoffel, W.; Ecker, W. " $\Delta^3$ -cis,  $\Delta^2$ -trans-Enoyl-CoA Isomerase from Rat Liver Mitochondria". In *Methods Enzymol.* 1969, XIV, 99-105.
- Tsuneya, T.; Ishihara, M.; Shiota, H.; Shiga, M. "Volatile Components of Quince Fruit (*Cydonia oblonga* Mill.)". *Agric. Biol. Chem.* 1983, 47, 2495-2502.
- Umano, K.; Shioji, A.; Hagi, Y.; Shibamoto, T. "Volatile Constituents of Peel of Quince Fruit, *Cydonia oblonga* Miller". *J. Agric. Food Chem.* 1986, 34, 593-596.

van Straten, S.; Maarse, H. In *Volatile Compounds in Food Qualitative Data*, 5th ed.; Division for Nutrition and Food Research TNO: Zeist, 1983; Section 81.2-81.5.

Winter, M.; Malet, G.; Pfeiffer, M.; Demole, E. "Structure d'Une Lactone Odorante Présente dans l'Essence de Jasmin (*Jasminum grandiflorum* L.)". *Helv. Chim. Acta* 1962, 45, 1250-1255.

Yabumoto, K.; Ingraham, D. F.; Jennings, W. G. "The Overload Phenomenon in Gas Chromatography". *HRC CC, J. High*

*Resolut. Chromatogr. Chromatogr. Commun.* 1980, 3, 248-252.

Yamanishi, T.; Kawatsu, M.; Yokoyama, T.; Nakatani, Y. "Methyl Jasmonate and Lactones Including Jasmine Lactone in Ceylon Tea". *Agric. Biol. Chem.* 1973, 37, 1075-1078.

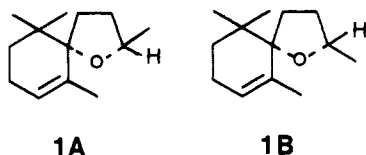
Received for review February 24, 1987. Revised manuscript received October 7, 1987. Accepted October 26, 1987. Names of products are included for the benefit of the reader and do not imply endorsement by USDA.

## 4-Hydroxy-7,8-dihydro- $\beta$ -ionol: Natural Precursor of Theaspiranes in Quince Fruit (*Cydonia oblonga*, Mill.)

Peter Winterhalter and Peter Schreier\*

In a polar fraction of an extract obtained from quince fruit juice (*Cydonia oblonga*, Mill.) by solvent extraction (pentane-dichloromethane, 2:1) and subsequent LC separation on silica gel, capillary gas chromatography (HRGC), and coupled HRGC techniques, i.e. on-line mass spectrometry (HRGC-MS) and Fourier transform infrared spectroscopy (HRGC-FTIR), the occurrence of 4-hydroxy-7,8-dihydro- $\beta$ -ionol was revealed. The identification was verified by comparison of HRGC, HRGC-MS, and HRGC-FTIR data of the natural product with those of an authentic reference compound synthesized from 4-oxo- $\beta$ -ionol. Model reactions carried out with 4-hydroxy-7,8-dihydro- $\beta$ -ionol under high-vacuum distillation/extraction conditions (40 °C, 5 h) showed the easy formation of theaspiranes at pH 3.5. The mechanism of theaspirane formation from 4-hydroxy-7,8-dihydro- $\beta$ -ionol can be considered as "prototropic dehydration of an allyl-1,6-diol" as previously described for monoterpene diols.

The diastereoisomeric spiro ethers theaspirane 1A and 1B have been found in raspberries (Winter and Enggist, 1971), yellow passion fruit (Winter and Klöti, 1972), black tea aroma (Renold et al., 1974), grapes (Schreier et al., 1976), *Osmanthus absolute* (Kaiser and Lamparsky, 1978), guava (Idstein and Schreier, 1985), black chokeberry (*Aronia melanocarpa* Ell.) (Hirvi and Honkanen, 1985), and quince fruit (Tsuneya et al., 1983; Winterhalter et al., 1987). Ether 1A possesses a fresh green and woody-



camphorous odor, characteristic of many oxygenated bicyclic monoterpenes, whereas this note almost becomes naphthalene-like in the diastereoisomeric ether 1B (Skorianetz et al., 1975; Ohloff, 1978). The theaspiranes are widely used in the flavor industry. In tobacco only 5 ppb suffice to reach the optimum flavor, and in order to round off fruit flavors, 1 ppb in the finished product is sufficient (Naegeli, 1977). Starting from ionone derivatives, several syntheses for 1A/1B have been described (Nakatani and Yamanishi, 1969; Ina et al., 1972; Naegeli, 1977; Etoh et al., 1980).

In our recent work on quince flavor (Winterhalter et al., 1987) it was demonstrated that 1A/1B were obviously not original volatiles but were formed at natural pH of the fruit pulp, i.e. under acidic conditions (pH 3.5-3.8) from a labile precursor. In this paper, we report the isolation and identification of this natural precursor of 1A/1B.

### EXPERIMENTAL SECTION

**Fruits.** Fresh ripe quince fruits (*Cydonia oblonga*, Mill.) were available from the local market.

**Sample Preparation.** Freshly prepared juice was obtained from 10 kg of cut fruits (seeds removed) after crushing and pressing (Hafico press). The juice (8.5 kg) was diluted with distilled water (1:1, v/v) and subjected to solvent extraction using pentane-dichloromethane (2:1) over 24 h (Drawert and Rapp, 1968). The extract was dried over anhydrous sodium sulfate and carefully concentrated to 1 mL on a Vigreux column (45 °C). The extract was fractionated on silica gel 60 (Merck), activity grade II, by applying a pentane-diethyl ether gradient. Cooled (11-13 °C) glass columns, 2 cm (i.d.)  $\times$  40 cm, were used. The elution rate was 120 mL/h, and seven fractions were separated: fraction I, 500 mL of pentane-diethyl ether (4:1, v/v); fraction II, 500 mL of pentane-diethyl ether (1:1, v/v); fraction III, 500 mL of pentane-diethyl ether (1:4, v/v); fractions IV.1-IV.4, each 250 mL of diethyl ether. All eluates were dried over anhydrous sodium sulfate and concentrated to 0.5 mL (for HRGC and HRGC-MS study) and to 0.1 mL (for HRGC-FTIR analysis), respectively.

**Synthesis of retro- $\alpha$ -ionols.** *a. Preparation of retro- $\alpha$ -ionones.* A solution of 17.2 g of  $\beta$ -ionone in 80 mL of dimethyl sulfoxide (cooled to -10 °C) was treated with 6 g of powdered sodium methoxide. After being stirred for 1 h at room temperature, the mixture was poured into ice and extracted twice with 250 mL of pentane. After the mixture was dried over anhydrous sodium sulfate and solvent removed, distillation gave 11 g of the isomeric retro- $\alpha$ -ionones (1:4 isomers about the exocyclic double bond): <sup>1</sup>H NMR (60 MHz, CDCl<sub>3</sub>), in close agreement with published data (Rosenberger et al., 1980); FTIR (vapor phase,  $\nu$ , cm<sup>-1</sup>) 3006, 2965, 2929, 1732, 1452, 1359, 1205, 1156, 871; EIMS *m/z* (%) isomer 1 (*R*<sub>t</sub> 1437) 43 (100) 55(28) 69 (48) 79 (23) 93 (52) 107 (51) 121 (52) 134 (5) 149 (28) 159 (3) 174 (2) 177 (2) 192 (13, M<sup>+</sup>); EIMS *m/z* (%)

Lehrstuhl für Lebensmittelchemie, Universität Würzburg, Am Hubland, D-8700 Würzburg, West Germany.