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ARTICLE *in* JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY · OCTOBER 1992

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# Volatile Constituents of Asian Pear (*Pyrus serotina*)

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The volatiles of Asian pear (Seuri cultivar) were studied by high-resolution gas chromatography and combined gas chromatography/mass spectrometry (GC/MS) using vacuum simultaneous distillation-extraction of blended fruit and dynamic headspace sampling of intact and enzymatically inhibited blended fruit. Esters were the dominant constituents in all of the samples. A total of 72 components were identified in the headspace of intact fruit, including 39 constituents reported for the first time in pear. Odor unit values calculated from concentration and odor threshold data indicate that the following compounds are important contributors to pear aroma: ethyl 2-methylbutanoate, ethyl hexanoate, ethyl butanoate, ethyl 2-methylpropanoate, hexyl acetate, ethyl heptanoate, hexanal, ethyl pentanoate, and ethyl propanoate.

Asian pears (*Pyrus serotina*) are a completely distinct species from the more common European-type pears (*Pyrus communis* L.) such as Bartlett and La France and are not a cross between apples and pears. Though the volatile constituents of Bartlett pears have been extensively investigated (Maarse and Visscher, 1984), there has been, to our knowledge, only one publication on the flavor compounds of Asian pears (Shiota et al., 1981). These researchers studied four Asian pear cultivars [Nijisseiki (20th Century), Kosui, Hosui, and Kikusui] and found distinct compositional differences between the peel and pulp. The peel contained major amounts of nonanal,  $\alpha$ -farnesene, phenylacetaldehyde, and straight-chain hydrocarbons with 19-23 carbon atoms, while the pulp had ethyl butanoate, hexanol, hexyl acetate, butylbenzene, and

phenylacetaldehyde as major constituents. The flavor of pears was recently reviewed by Paillard (1990).

## EXPERIMENTAL PROCEDURES

**Materials. Sample Preparation.** 1. *Vacuum Simultaneous Distillation-Extraction (Vacuum SDE).* The skin and pulp (1.0 kg, core and seeds were excluded) were blended with 500 mL of water in a Waring blender for 20 s. Three batches were prepared using a total of 3.0 kg of fruit pulp and skin. The slurry was added to a 12 L round-bottomed flask. An additional 1.5 L of water and 60 mL of antifoam solution were added to the flask. The antifoam solution was prepared by adding 7 mL of Hartwick antifoam 50 emulsion to 1000 mL of water and boiling until the volume was reduced to ca. 700 mL to remove volatiles. Vacuum SDE was performed (58 mmHg) for 2 h using hexane and the SDE head described by Schultz et al. (1977). The resulting extract

Table I. Volatile Constituents of Asian Pear: Vacuum Steam Distillation-Extraction

constituent	JDB-1		% area <sup>a</sup>	constituent	JDB-1		% area <sup>a</sup>
	exptl	ref			exptl	ref	
ethyl propanoate	693	692	0.28	ethyl 3-(methylthio)-(E)-2-propanoate <sup>b</sup> + unknown	1143	1144	0.06
ethyl 2-methylpropanoate	751	738	0.17	$\alpha$ -terpineol	1169	1170	0.02
2-methylpropyl acetate	764	764	0.04	ethyl (E)-4-octenoate <sup>b</sup>	1172	1169	0.04
methyl 2-methylbutanoate <sup>b</sup>	767	768	0.08	butyl hexanoate	1176	1173	0.06
hexanal	781	778	7.83	hexyl butanoate	1178	1175	0.32
ethyl butanoate	793	789	18.71	ethyl octanoate	1184	1180	1.59
butyl acetate	804	796	8.72	octyl acetate	1196	1193	0.56
(E)-2-hexenal	829	827	1.24	2-phenylethyl acetate <sup>b</sup> + hexyl 2-methylbutanoate <sup>b</sup>	1224	1224	
ethyl 2-methylbutanoate <sup>b</sup>	843	842	1.73		1224	1222	0.05
hexanol	866	860	9.01	ethyl (E)-2-octenoate	1225	1223	0.06
3-methylbutyl acetate	867	866	0.19	(E)-3-decen-1-ol <sup>b</sup>	1233	1233	0.49
2-methylbutyl acetate	869	869	0.04	(Z)-4-decen-1-ol <sup>b</sup>	1242	1241	1.95
propyl butanoate <sup>b</sup>	886	879	0.05	decanol	1258	1255	0.36
ethyl pentanoate <sup>b</sup>	888	881	0.31	(2,4-decadienal) <sup>c</sup>	1267		0.03
pentyl acetate	899	895	0.37	(E,E)-2,4-decadienal	1286	1286	0.03
methyl hexanoate <sup>b</sup>	910	906	0.63	biphenyl	1345	1349	1.12
ethyl tiglate <sup>b</sup>	924	923	0.07	ethyl (Z)-4-decenoate	1363	1361	0.19
heptanol	964	951	0.13	hexyl hexanoate + (methyl 2,4-decadienoate) + unknown	1371	1369	
butyl butanoate	983	977	0.06		1371	1370	0.83
ethyl hexanoate	990	986	14.49	octyl butanoate <sup>b</sup>	1374	1372	0.02
hexyl acetate	1004	995	20.83	(E)-3-decenyl acetate <sup>b</sup>	1376		0.09
phenylacetaldehyde	1008	1006	0.03	ethyl decanoate	1380	1379	0.07
ethyl (E)-2-hexenoate	1025	1020	0.02	decyl acetate <sup>b</sup>	1394	1393	0.08
octanol	1060	1053	1.21	ethyl (E,Z)-2,4-decadienoate (sesquiterpene HC) + (ethyl 2,4-decadienoate)	1447	1444	2.37
ethyl 3-(methylthio)propanoate <sup>b</sup>	1072	1069	0.12		1482		0.14
propyl hexanoate <sup>b</sup>	1081	1077	0.05	$\alpha$ -farnesene	1495	1496	0.91
ethyl heptanoate <sup>b</sup>	1084	1080	0.15	hexyl octanoate <sup>b</sup>	1566	1565	0.04
3-(methylthio)propyl acetate <sup>b</sup>	1091	1091	0.02				
heptyl acetate	1096	1094	0.20				
methyl octanoate	1108	1107	0.07				

<sup>a</sup> Peak area percentage of total FID area excluding the solvent peaks (assuming all response factors of 1). <sup>b</sup> Identified for the first time in pear. <sup>c</sup> Tentative or partial identifications enclosed in parentheses.

Table II. Volatile Constituents of Asian Pear: Dynamic Headspace Sampling of Intact Fruit

constituent	$J_{DB-1}$		% area <sup>a</sup>	constituent	$J_{DB-1}$		% area <sup>a</sup>
	exptl	ref			exptl	ref	
ethyl acetate	601	600	0.14	methyl ( <i>E</i> )-2-octenoate	1226	1223	0.13
ethyl propanoate	693	692	0.04	( <i>E</i> )-3-decen-1-ol <sup>b</sup>	1233	1233	0.29
propyl acetate	697	695	0.02	( <i>Z</i> )-4-decen-1-ol <sup>b</sup>	1243	1241	1.49
methyl butanoate <sup>b</sup>	708	705	0.07	decanol	1259	1255	0.38
ethyl 2-methylpropanoate	751	738	0.04	1-methylnaphthalene <sup>b</sup>	1263	1268	0.01
2-methylpropyl acetate	763	764	0.02	(2,4-decadienal) <sup>c</sup>	1267		0.04
methyl 2-methylbutanoate <sup>b</sup>	767	768	0.02	pentyl hexanoate <sup>b</sup>	1273	1270	tr
ethyl butanoate	791	789	4.65	propyl octanoate <sup>b</sup>	1277	1277	0.06
butyl acetate	802	796	3.17	ethyl nonanoate <sup>b</sup>	1281	1279	0.03
methyl pentanoate <sup>b</sup>	810	806	0.01	methyl ( <i>Z</i> )-4-decenoate	1290	1289	0.31
ethyl 2-butenolate <sup>b</sup>	827	819	0.02	nonyl acetate <sup>b</sup>	1295	1293	0.01
ethyl 2-methylbutanoate <sup>b</sup>	842	842	0.84	methyl decanoate	1308	1307	0.04
hexanol	861	860	0.29	eugenol <sup>b</sup>	1325	1326	0.03
3-methylbutyl acetate	866	866	0.13	2-methylpropyl octanoate <sup>b</sup>	1334	1334	0.01
2-methylbutyl acetate	868	869	0.06	biphenyl	1346	1349	1.38
propyl butanoate <sup>b</sup>	885	879	0.04	ethyl ( <i>Z</i> )-4-decenoate	1364	1361	1.80
ethyl pentanoate <sup>b</sup>	888	881	0.26	hexyl hexanoate +	1372	1370	
pentyl acetate	898	895	0.19	(methyl 2,4-decadienoate)	1372	1372	1.41
3-methylbut-2-enyl acetate <sup>b</sup>	905	902	0.01	octyl butanoate <sup>b</sup>	1372	1372	<i>d</i>
methyl hexanoate <sup>b</sup>	911	906	1.51	ethyl ( <i>E</i> )-3-decenoate <sup>b</sup>	1377	1374	0.15
ethyl tiglate <sup>b</sup>	924	923	0.04	ethyl decanoate	1382	1379	1.49
propyl 2-methylbutanoate <sup>b</sup>	936	936	0.01	(ethyl 2,4-decadienoate)	1417		0.03
2-methylpropyl butanoate <sup>b</sup>	945	937	0.01	(ethyl 2,4-decadienoate)	1432		0.01
heptanol	968	951	0.03	3-methylbutyl octanoate <sup>b</sup>	1435	1430	0.01
butyl butanoate		977	<i>d</i>	(ethyl decatrienoate)	1439		0.15
ethyl hexanoate	994	986	29.67	ethyl ( <i>E,Z</i> )-2,4-decadienoate	1449	1444	3.40
hexyl acetate	1006	995	14.34	valencene <sup>b</sup>	1481	1486	0.10
methyl heptanoate <sup>b</sup>	1011	1006	0.02	(sesquiterpene)	1483		0.16
ethyl ( <i>E</i> )-2-hexenoate <sup>b</sup>	1026	1020	0.02	(ethyl 2,4-decadienoate)	1483		<i>d</i>
octanol	1060	1053	0.56	$\alpha$ -farnesene	1500	1496	8.00
ethyl 3-(methylthio)propanoate <sup>b</sup>	1072	1069	0.06	pentadecane <sup>b</sup>	1503	1500	0.01
propyl hexanoate <sup>b</sup>	1081	1077	0.10	ethyl dodecanoate	1579	1578	0.07
ethyl heptanoate <sup>b</sup>	1084	1080	0.33	hexadecane <sup>b</sup>	1600	1600	0.02
hexyl propanoate <sup>b</sup> +	1091	1088		heptadecane	1700	1700	0.04
3-(methylthio)propyl acetate <sup>b</sup>	1091	1091	0.01	ethyl tetradecanoate	1780	1778	0.05
heptyl acetate	1096	1094	0.20	octadecane	1800	1800	0.01
ethyl 3-hydroxyhexanoate <sup>b</sup>	1103	1103	tr	nonadecane	1900	1900	0.01
methyl octanoate	1109	1107	0.89	ethyl hexadecanoate <sup>b</sup>	1978	1978	0.01
2-methylpropyl hexanoate <sup>b</sup>	1138	1138	0.02				
ethyl benzoate <sup>b</sup> +	1143	1143					
ethyl 3-(methylthio)-( <i>E</i> )-	1143	1144	0.03				
2-propenoate <sup>b</sup>							

<sup>a</sup> Peak area percentage of total FID area excluding the solvent peaks (assuming all response factors of 1). tr indicates percent area less than 0.01%. <sup>b</sup> Identified for the first time in pear. <sup>c</sup> Tentative or partial identifications enclosed in parentheses. <sup>d</sup> Peak elutes as a shoulder on adjacent peak.

was chilled to -20 °C to freeze out residual water. The extract was quickly decanted and then concentrated under reduced pressure (58 mmHg) with a Vigreux column to a final volume of 0.8–1.0 mL.

**2. Dynamic Headspace Sampling of Intact Fruit.** Intact fruit (total weight 3.94 kg) were placed in a 9-L Pyrex glass container. A Pyrex glass head was attached to the top of the container which allowed purified air to enter the bottom of the chamber and exit through a Tenax trap [consisting of a glass tube 14 cm × 2.2 cm (i.d.) which terminated in ball and socket joints; 10 g of Tenax (Alltech Associates, Deerfield, IL)]. Sampling was continued at room temperature (ca. 27 °C) for 24 h at 3 L/min. The collected volatiles were eluted from the trap with freshly distilled diethyl ether containing 0.001% Ethyl antioxidant 330 [1,3,5-trimethyl-2,4,6-tris(3,5-di-*tert*-butyl-4-hydroxybenzyl)benzene; Ethyl Corp., Baton Rouge, LA] and carefully concentrated with a Vigreux column to a final volume of ca. 100  $\mu$ L.

**3. Dynamic Headspace Sampling of Blended Fruit.** The skin and pulp of washed fruit (200 g; 50 g from four different fruit) were blended with 200 mL of saturated CaCl<sub>2</sub> solution for 30 s in a Waring blender. 3-Octanone (10 mL of a water solution containing 20 ppm) was added as an internal standard, and the mixture was blended for an additional 15 s. The slurry was added to a 1-L round-bottom flask. A Pyrex head was attached to the top of the flask which allowed purified air to pass over the surface of the slurry (via a Teflon tube) and exit out of the top through a Tenax trap (dimensions as cited above). Sampling was continued at room temperature (ca. 27 °C) for 2 h at 3 L/min.

The collected volatiles were eluted from the trap with 100 mL of freshly distilled diethyl ether containing 0.001% Ethyl antioxidant 330 and carefully concentrated with a Vigreux column to a final volume of ca. 100  $\mu$ L.

**Gas Chromatography.** A Hewlett-Packard (Avondale, PA) 5890 gas chromatograph equipped with a 60 m × 0.32 mm i.d. DB-1 fused silica capillary column ( $d_f$  = 0.25  $\mu$ m; J&W Scientific, Folsom, CA) and a flame ionization detector (FID) was employed. The injector and detector temperatures were 180 and 270 °C, respectively. Helium was used as the carrier gas at an average linear velocity ( $\mu$ ) of 34 cm/s (30 °C). The oven temperature was programmed from 30 (4 min isothermal) to 210 °C at 2 °C/min. The split ratio was 1:26. An HP 5895 GC ChemStation was used for data processing.

**Gas Chromatography/Mass Spectrometry (GC/MS).** A Finnigan MAT (San Jose, CA) 4500 GC/MS/INCOS system (quadrupole) equipped with the same type of column used in the GC analyses was employed. Split injection (1:25) was used. The oven temperature was programmed from 50 to 210 °C at 2 °C/min. Helium carrier gas was used at a column head pressure of 15 psi. The instrument was operated in the electron impact mode at 70 eV, taking scans from 33 to 350  $m/z$  in a 1-s cycle.

**Chiral Analysis of Ethyl 2-Methylbutanoate.** Ethyl 2-methylbutanoate was isolated from pear extract obtained by vacuum SDE using preparative gas chromatography. The enriched fractions were subsequently introduced into a HP 5890 Series II gas chromatograph equipped with a FID and a permethylated  $\beta$ -cyclodextrin fused silica capillary column [60

Table III. Volatile Constituents of Asian Pear: Dynamic Headspace Sampling of Blended Fruit

constituent	$I_{DB-1}^a$		approx concn, <sup>a</sup> ppb	constituent	$I_{DB-1}^a$		approx concn, <sup>a</sup> ppb
	exptl	ref			exptl	ref	
ethyl propanoate	694	692	263	ethyl heptanoate <sup>b</sup>	1084	1080	87
ethyl 2-methylpropanoate	750	738	76	3-(methylthio)propyl acetate <sup>b</sup>	1091	1091	tr
2-methylpropyl acetate	763	764	32	heptyl acetate	1096	1094	20
hexanal	779	778	189	methyl octanoate	1108	1107	4
ethyl butanoate	792	789	4756	ethyl 3-(methylthio)-(E)-	1143	1144	4
butyl acetate	801	796	879	2-propenoate <sup>b</sup>			
(E)-2-hexenal	827	827	127	ethyl (E)-4-octenoate <sup>b</sup>	1173	1169	47
ethyl 2-methylbutanoate <sup>b</sup>	842	842	222	butyl hexanoate	1176	1173	6
hexanol	860	860	109	hexyl butanoate	1178	1175	122
3-methylbutyl acetate	865	866	27	ethyl octanoate	1184	1180	608
2-methylbutyl acetate	868	869	30	octyl acetate	1195	1193	47
propyl butanoate <sup>b</sup>	885	879	17	ethyl (E)-2-octenoate	1225	1223	22
ethyl pentanoate <sup>b</sup>	887	881	139	(E)-3-decen-1-ol <sup>b</sup>	1232	1233	4
pentyl acetate	898	895	38	(Z)-4-decen-1-ol <sup>b</sup>	1240	1241	22
methyl hexanoate <sup>b</sup>	909	906	85	(2,4-decadienal)	1266		7
ethyl tiglate <sup>b</sup>	923	923	6	methyl (Z)-4-decenoate	1290	1289	4
2-methylpropyl butanoate	945	937	2	ethyl (Z)-4-decenoate	1363	1361	279
ethyl hexanoate	991	986	9427	hexyl hexanoate +	1370	1369	
hexyl acetate	1000	995	984	(methyl 2,4-decadienoate) <sup>c</sup>	1370	1370	67
ethyl (E)-2-hexenoate <sup>b</sup>	1024	1020	16	octyl butanoate <sup>b</sup>	1372	1372	tr
octanol	1059	1053	31	ethyl decanoate	1380	1379	5
ethyl 3-(methylthio)propanoate <sup>b</sup>	1071	1069	8	ethyl (E,Z)-2,4-decadienoate	1447	1444	604
propyl hexanoate <sup>b</sup>	1080	1077	20	$\alpha$ -farnesene	1495	1496	110

<sup>a</sup> Only approximate concentrations since percent recoveries and FID response factors were not determined for each compound (assume all response factors of 1). tr represents concentration less than 1 ppb. <sup>b</sup> Identified for the first time in pear. <sup>c</sup> Tentative or partial identifications enclosed in parentheses.

m  $\times$  0.32 mm (i.d.) coated with 10% heptakis(2,3,6-tri-*O*-methyl)- $\beta$ -cyclodextrin in 1701 (7% cyanopropyl, 7% phenyl, 86% dimethylpolysiloxane)]. Split injection (1:35) was employed. The column oven was held isothermally at 30 °C. Helium carrier gas was used at an average linear velocity ( $\mu$ ) of 27.4 cm/s (30 °C). Injector and detector temperatures were 175 and 280 °C, respectively.

**Reference Compounds.** Reference standards were obtained from commercial sources or synthesized according to established procedures. (Z)-4-Decen-1-ol had the following mass spectrum: 138 (9), 110 (13), 109 (14), 96 (21), 95 (31), 83 (16), 82 (50), 81 (84), 79 (27), 71 (11), 69 (32), 68 (79), 67 (100), 57 (20), 56 (21), 55 (74), 54 (49), 53 (31), 43 (25), 41 (94). (E)-3-Decenyl acetate, prepared by the acetylation of 3-decen-1-ol, had the following mass spectrum: 138 (19), 110 (20), 109 (12), 96 (23), 95 (13), 82 (23), 81 (37), 68 (30), 67 (48), 55 (28), 54 (49), 43 (100), 41 (27).

**Odor Threshold Determinations.** Odor thresholds were determined with a panel of 16–20 persons using compounds purified by preparative gas chromatography.

## RESULTS AND DISCUSSION

The volatile constituents of Asian pear were isolated using vacuum steam distillation-extraction (vacuum SDE) and dynamic headspace sampling of intact and blended fruit. The samples were analyzed by high-resolution gas chromatography and combined gas chromatography/mass spectrometry (GC/MS). Sample constituents were identified by comparing the compound's mass spectrum and Kovats retention index, *I* (Kovats, 1958), with that of an authentic reference standard.

Table I lists the volatiles identified in the vacuum SDE sample. Esters comprised more than 73% of the total volatiles. The major esters included hexyl acetate (20.83%), ethyl butanoate (18.71%), ethyl hexanoate (14.49%), butyl acetate (8.72%), ethyl (E,Z)-2,4-decadienoate (2.37%), ethyl 2-methylbutanoate (1.73%), and ethyl octanoate (1.59%). Ethyl (E,Z)-2,4-decadienoate, the character impact compound of Bartlett pear (Jennings et al., 1964), was previously identified in Asian pear peel, although it was not found in the fruit flesh (Shiota et al., 1981). This ester was not present in La France pear, although the corresponding *E,E* isomer was found (Shiota, 1990). The sulfur-containing esters, ethyl 3-(methylthio)-

propanoate, 3-(methylthio)propyl acetate, and ethyl 3-(methylthio)-(E)-2-propenoate, are reported for the first time in pears. The first compound is a well-known pineapple constituent (Takeoka et al., 1989) and has also been reported in Concord grape essence (Winter et al., 1990). The second and third compounds have been recently identified in pineapple (Takeoka et al., 1989, 1991). Though not found in this sample, the structurally related sulfur-containing aldehyde, 3-(methylthio)propanal, was previously identified in Asian pear peel (Shiota et al., 1981). Ethyl tiglate [ethyl (E)-2-methyl-2-butenate] is reported for the first time in pear. The tiglates are less common plant volatiles (Idstein and Schreier, 1985), with the butyl ester being reported in Roman camomile oil (Windholz, 1976) and Alphonso mango (Idstein and Schreier, 1985). As there was not attempt to deactivate the enzymes during disruption of fruit tissues, high levels of the C<sub>6</sub> lipid peroxidation products, hexanal (7.83%), (E)-2-hexenal (1.24%), and hexanol (9.01%), were produced (Grosch, 1982). Biphenyl probably originates from its use as a fungistat, although this fruit was reportedly not treated with any chemicals.

The volatiles obtained by dynamic headspace sampling of intact fruit are listed in Table II. The percent area values should be considered as approximate since sample constituents coeluted with solvent peaks and sample breakthrough was not determined. Esters constituted over 66% of the volatiles with large amounts of the following: ethyl hexanoate (29.67%), hexyl acetate (14.34%), ethyl butanoate (4.65%), ethyl (E,Z)-2,4-decadienoate (3.40%), butyl acetate (3.17%), and ethyl (Z)-4-decenoate (1.80%), methyl hexanoate (1.51%), and ethyl decanoate (1.49%).  $\alpha$ -Farnesene was previously found as the dominant constituent in Asian pear peel (Shiota et al., 1981). Eugenol was recently identified as both a free and bound constituent in white-fleshed nectarine (Takeoka et al., 1992). In contrast to the esters of La France pear (Shiota et al., 1990), which consisted primarily of acetates, Seuri contained a wider variety including propanoates, butanoates, 2-methylbutanoates, pentanoates, hexanoates, heptanoates, and octanoates. While pentyl 2-methylbutanoate has been

Table IV. Approximate Concentrations, Odor Thresholds in Water, and Odor Units of Some Asian Pear Constituents

constituent <sup>a</sup>	approx concn, <sup>b</sup> μg/kg	odor threshold, <sup>c</sup> ppb	odor units, <sup>d</sup> U <sub>0</sub>	constituent <sup>a</sup>	approx concn, <sup>b</sup> μg/kg	odor threshold, <sup>c</sup> ppb	odor units, <sup>d</sup> U <sub>0</sub>
ethyl 2-methylbutanoate	222	0.006 <sup>e</sup>	37000	2-methylbutyl acetate	30	11	2.7
ethyl hexanoate	9427	1	9427	ethyl 3-(methylthio)propanoate	8	7 <sup>i</sup>	1.1
ethyl butanoate	4756	1 <sup>e</sup>	4756	methyl hexanoate	85	84 <sup>h</sup>	1.0
ethyl 2-methylpropanoate	76	0.1 <sup>f</sup>	760	ethyl (E)-4-octenoate	47	50	0.9
hexyl acetate	984	2 <sup>f</sup>	492	hexyl butanoate	122	250 <sup>h</sup>	0.5
ethyl heptanoate	87	2.2 <sup>h</sup>	39.5	2-methylpropyl acetate	32	65	0.5
hexanal	189	5 <sup>i</sup>	37.8	octanol	31	110	0.3
ethyl pentanoate	139	5 <sup>e</sup>	27.8	propyl butanoate	17	124	0.1
ethyl propanoate	263	10	26.3	ethyl tiglate	6	65	0.1
3-methylbutyl acetate	27	2	13.5	hexanol	109	2500 <sup>h</sup>	0.04
butyl acetate	879	66 <sup>e</sup>	13.3	ethyl decanoate	5	122	0.04
(E)-2-hexenal	127	17 <sup>i</sup>	7.5	methyl octanoate	4	200	0.02
ethyl octanoate	608	92	6.6	ethyl 3-(methylthio)-(E)- 2-propenoate	4	246 <sup>h</sup>	0.016
ethyl (E,Z)-2,4-decadienoate	604	100 <sup>i</sup>	6.0	butyl hexanoate	6	700 <sup>h</sup>	0.009
octyl acetate	47	12	3.9				

<sup>a</sup> The constituents were isolated by dynamic headspace sampling of blended fruit (in saturated CaCl<sub>2</sub> solution) and are listed in descending order of their odor units. <sup>b</sup> Concentrations were determined with use of an internal standard and should only be considered as approximate since percent recoveries and FID response factors were not determined for each compound (assume all response factors of 1). <sup>c</sup> Odor threshold in water. <sup>d</sup> U<sub>0</sub> = compound concentration divided by its odor threshold. <sup>e</sup> Odor threshold of the S enantiomer; this Asian pear cultivar was found to contain exclusively the S enantiomer. <sup>f</sup> Buttery et al. (1982). <sup>g</sup> Flath et al. (1967). <sup>h</sup> Takeoka et al. (1990b). <sup>i</sup> Buttery et al. (1987). <sup>j</sup> Takeoka et al. (1989). <sup>k</sup> Takeoka et al. (1991). <sup>l</sup> Approximate odor threshold since compound was only 95% pure.

previously identified in pear (Maarse and Visscher, 1981), the corresponding methyl, ethyl, propyl, and hexyl esters are reported for the first time in pear.

Table III shows the volatile constituents obtained by dynamic headspace sampling of blended fruit. The fruit was blended in saturated CaCl<sub>2</sub> solution to inhibit enzymatic action. Approximate concentrations were determined through the use of 3-octanone as an internal standard. 1-(E,Z)-3,5-Undecatriene, a compound previously identified in Bartlett pear (Berger et al., 1985), was not detected in any of the samples.

The relative contribution of various constituents to the overall pear aroma was determined by calculating the number of odor units (U<sub>0</sub>). Guadagni et al. (1966) defined the odor unit as the compound concentration divided by its odor threshold. Table IV lists the odor units of some pear constituents along with odor thresholds and approximate concentrations. Compounds are listed in descending order of their odor unit values. Due to its particularly low odor threshold of 0.006 ppb, ethyl 2-methylbutanoate appears to be an important contributor to pear aroma. The dominant role of esters to the odor is clear as other important contributors include ethyl hexanoate, ethyl butanoate, ethyl 2-methylpropanoate, hexyl acetate, ethyl heptanoate, hexanal, ethyl pentanoate, ethyl propanoate, 3-methylbutyl acetate, and butyl acetate. Despite the use of preparative gas chromatography, ethyl (E,Z)-2,4-decadienoate could only be purified to 95% due to the presence of closely eluting isomers. The odor threshold of the partially purified ester was determined to be 100 ppb. The approximate concentration of this ester in Asian pear is 604 ppb. Therefore, its odor unit value is only 6, which makes it a relatively small contributor to Asian pear aroma.

Fractions enriched in ethyl 2-methylbutanoate were collected using preparative gas chromatography and subsequently chromatographed on a permethylated β-cyclodextrin capillary column. Analysis of fresh pear extract obtained by vacuum SDE revealed that ethyl 2-methylbutanoate occurred in exclusively the S-+ configuration. Earlier studies had shown that this important ester is also present in exclusively the S-+ configuration in pineapple (Takeoka et al., 1990) and predominantly in the S-+ configuration in Granny Smith apples (Mosandl et al., 1991).

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- tanoate, 105-66-8; ethyl pentanoate, 539-82-2; pentyl acetate, 628-63-7; methyl hexanoate, 106-70-7; ethyl tiglate, 5837-78-5; heptanol, 111-70-6; butyl butanoate, 109-21-7; ethyl hexanoate, 123-66-0; hexyl acetate, 142-92-7; phenylacetaldehyde, 122-78-1; ethyl (*E*)-2-hexenoate, 27829-72-7; octanol, 111-87-5; ethyl 3-(methylthio)propanoate, 13327-56-5; propyl hexanoate, 626-77-7; ethyl heptanoate, 106-30-9; 3-(methylthio)propyl acetate, 16630-55-0; heptyl acetate, 112-06-1; methyl octanoate, 111-11-5; ethyl 3-(methylthio)-(*E*)-2-propenoate, 136115-65-6;  $\alpha$ -terpineol, 98-55-5; ethyl (*E*)-4-octenoate, 78989-37-4; butyl hexanoate, 626-82-4; hexyl butanoate, 2639-63-6; ethyl octanoate, 106-32-1; octyl acetate, 112-14-1; 2-phenylethyl acetate, 103-45-7; hexyl 2-methylbutanoate, 10032-15-2; ethyl (*E*)-2-octenoate, 7367-82-0; (*E*)-3-decen-1-ol, 18409-18-2; (*Z*)-4-decen-1-ol, 57074-37-0; decanol, 112-30-1; 2,4-decadienal, 2363-88-4; (*E,E*)-2,4-decadienal, 25152-84-5; biphenyl, 92-52-4; ethyl (*Z*)-4-decenoate, 7367-84-2; hexyl hexanoate, 6378-65-0; methyl 2,4-decadienoate, 53172-59-1; octyl butanoate, 110-39-4; (*E*)-3-decenyl acetate, 81634-98-2; ethyl decanoate, 110-38-3; decyl acetate, 112-17-4; ethyl (*E,Z*)-2,4-decadienoate, 3025-30-7; ethyl 2,4-decadienoate, 37549-74-9;  $\alpha$ -farnesene, 502-61-4; hexyl octanoate, 1117-55-1; ethyl acetate, 141-78-6; propyl acetate, 109-60-4; methyl butanoate, 623-42-7; methyl pentanoate, 624-24-8; ethyl 2-butenate, 10544-63-5; 3-methylbut-2-enyl acetate, 1191-16-8; propyl 2-methylbutanoate, 37064-20-3; 2-methylpropyl butanoate, 539-90-2; methyl heptanoate, 106-73-0; hexyl propanoate, 2445-76-3; ethyl 3-hydroxyhexanoate, 2305-25-1; 2-methylpropyl hexanoate, 105-79-3; ethyl benzoate, 93-89-0; methyl (*E*)-2-octenoate, 7367-81-9; 1-methylnaphthalene, 90-12-0; pentyl hexanoate, 540-07-8; propyl octanoate, 624-13-5; ethyl nonanoate, 123-29-5; methyl (*Z*)-4-decenoate, 7367-83-1; nonyl acetate, 143-13-5; methyl decanoate, 110-42-9; eugenol, 97-53-0; 2-methylpropyl octanoate, 5461-06-3; ethyl (*E*)-3-decenoate, 82561-67-9; ethyl 2,4-decadienoate, 37549-74-9; 3-methylbutyl octanoate, 2035-99-6; ethyl decatrienoate, 143371-40-8; valencene, 4630-07-3; pentadecane, 629-62-9; hexadecane, 544-76-3; heptadecane, 629-78-7; ethyl tetradeconoate, 124-06-1; octadecane, 593-45-3; nonadecane, 629-92-5; ethyl hexadecanoate, 628-97-7.

Received for review May 28, 1992. Accepted July 27, 1992.

**Registry No.** Ethyl propanoate, 105-37-3; ethyl 2-methylpropanoate, 97-62-1; 2-methylpropyl acetate, 110-19-0; methyl 2-methylbutanoate, 868-57-5; hexanal, 66-25-1; ethyl butanoate, 105-54-4; butyl acetate, 123-86-4; (*E*)-2-hexenal, 6728-26-3; ethyl 2-methylbutanoate, 7452-79-1; hexanol, 111-27-3; 3-methylbutyl acetate, 123-92-2; 2-methylbutyl acetate, 624-41-9; propyl bu-