

$\gamma$ -dodecalactone, the yeast reduction product is nearly optically pure and (4*R*)-configured (Gessner et al., 1987). For the case of 3,4-dimethyl  $\gamma$ -lactone the odor activity depends on geometric as well as optical isomerism (Table VI). The (4*S*)-configured isomer is much more intense as the (4*R*)-isomer in both the cis and trans series. This means that chirality is of special importance for odor intensity. On the other hand, odor quality seems to be mainly influenced by geometric isomerism. While the odor quality of 3,4-dimethyl  $\gamma$ -lactone stereoisomers is different between the cis and trans series, the intensities of taste within cis and trans series, respectively, are comparable.

Research on chirality evaluation of natural occurring  $\gamma$ -lactones in fruits is still under investigation.

#### ACKNOWLEDGMENT

We are indebted to the Deutsche Forschungsgemeinschaft and to the Bundesministerium für Jugend, Familie, Frauen und Gesundheit, for financial support.

**Registry No.** 1, 58917-25-2; 1', 19041-15-7; 2, 63357-95-9; 2', 41035-07-8; 3, 88270-38-6; 3', 31323-51-0; 4, 107797-24-0; 4', 107797-25-1; 5, 63357-96-0; 5', 63357-97-1; 6, 107797-26-2; 6', 107797-27-3; 7, 74568-06-2; 7', 74568-05-1; 8, 69830-91-7; 8', 69830-92-8; 9, 90026-55-4; 9', 80009-59-2; 10, 90026-46-3; 10', 110171-22-7; 11, 118437-75-5; 11', 118437-76-6; 12, 118437-77-7; 12', 118437-78-8; 13, 118437-79-9; 13', 118437-80-2; 14, 118437-81-3; 14', 118437-82-4; 15, 118437-83-5; 15', 118437-84-6; 16, 118437-85-7; 16', 118437-86-8; 17, 118437-87-9; 17', 118437-88-0; 18, 118437-89-1; 18', 118437-90-4; 19, 118437-91-5; 19', 118492-34-5; 20, 118492-35-6; 20', 118492-36-7; 21, 118437-92-6; 21', 118492-37-8; 22, 118437-93-7; 22', 118492-38-9; 23, 118437-94-8; 23', 118492-39-0; 24, 118437-95-9; 24', 118492-40-3; 25, 118437-96-0; 25', 118492-41-4; 26, 118437-97-1; 26', 118492-42-5; 27, 118437-98-2; 27', 118492-43-6; 28, 118437-99-3; 28', 118492-44-7; 29, 118438-00-9; 29', 118492-45-8; 30, 118492-46-9; 30', 118492-47-0; I, 7782-26-5; II, 13429-83-9; II (acid chloride), 39637-74-6; isopropyl ( $\pm$ )-4-hydroxypentanoate, 118438-01-0; isopropyl ( $\pm$ )-4-hydroxyhexanoate, 118438-02-1; isopropyl ( $\pm$ )-4-hydroxyheptanoate, 118438-03-2; isopropyl ( $\pm$ )-4-hydroxyoctanoate, 118438-04-3; isopropyl ( $\pm$ )-4-hydroxynonanoate, 118438-05-4; isopropyl ( $\pm$ )-4-hydroxydecanoate, 118438-06-5; isopropyl ( $\pm$ )-4-hydroxyundecanoate, 118438-07-6; isopropyl ( $\pm$ )-4-hydroxydodecanoate, 118438-08-7; 2-bromopropane, 75-26-3; (R)-2-phenylpropionic acid chloride, 36240-11-6.

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Received for review September 2, 1987. Accepted July 20, 1988.

## Volatile Components of Bittermelon

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Volatile components of bittermelon (*Momordica charantia* L.) fruit and bittermelon vines were identified by gas chromatography-mass spectrometry. Major constituents were myrtenol, *cis*-hex-3-enol, benzyl alcohol, pent-1-en-3-ol, *cis*-pent-2-enol, and *trans*-hex-2-enal. *cis*-Sabinol was identified as a naturally occurring compound. Bittermelon volatiles are attractive to the melon fly, *Dacus cucurbitae*.

Bittermelon, *Momordica charantia* L., is a major host for the melon fly, *Dacus cucurbitae* Coquillett (Diptera: Tephritidae). In Hawaii, bittermelon was more frequently infested by this fly than watermelon, squash, tomato, and cucumber, other major hosts (Harris et al., 1986). In Ta-

iwai, the population density of melon flies in a bittermelon field was greater than in litchi, pear, loquat, and grape fields (Fang and Chang, 1984), and the population buildup of the melon fly in Punjab was bolstered by bittermelon (Bains and Sidhu, 1984).

Our study of bittermelon volatile compounds was undertaken because we seek to identify compounds attractive to the melon fly for use in population monitoring and control programs.

There is no previous study of bittermelon volatiles, but

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other members of the Cucurbitaceae tribe have been investigated. These include cucumber (Forss et al., 1962; Kemp et al., 1974a), honeydew melon (Buttery et al., 1982), muskmelon (Kemp et al., 1972a,b, 1974b; Yabumoto et al., 1977), watermelon (Kemp et al., 1974b; Kemp, 1975; Yajima et al., 1985), and squash blossoms (Andersen, 1987). Indole found in squash blossoms was a potent attractant for the western corn rootworm and the striped cucumber beetle (Andersen and Metcalf, 1986).

#### EXPERIMENTAL SECTION

**Starting Materials.** Bittermelons and bittermelon vines were purchased in northern California produce markets at various times during the growing season. They were either processed immediately for solvent extraction or kept refrigerated in plastic bags for no longer than 2 days. Some bittermelons were frozen at  $-20^{\circ}\text{C}$  and subsequently freeze-dried.

**Isolation of Volatiles.** Bittermelons (2 kg) or bittermelon vines (2 kg) were cut up and then blended with distilled acetone in a 1-gal stainless steel Waring Blender. The mixture was filtered, and the filter cake was rinsed with acetone before being reblended with fresh solvent. Acetone was removed from the extract by distillation under reduced pressure and was collected in a flask chilled by solid carbon dioxide. Distillation through a packed column at atmospheric pressure removed most of the acetone from the acetone distillate and left a watery solution of bittermelon extract volatiles. Water was added to the extract from which acetone had been distilled, and the mixture was vacuum steam distilled at a pressure of 25 mmHg. The steam distillate and the residue from the acetone distillation were combined, saturated with salt, and extracted with freshly distilled ether. The ether extract was dried with sodium sulfate and then concentrated by distillation of ether to a volume of about two mL.

Ice collected from freeze-drying of bittermelons was thawed. The aqueous solution of volatiles was saturated with salt and extracted with distilled ether. The ether extract was dried by sodium sulfate and then concentrated by distillation of ether. Volatiles thus obtained were compared with volatiles obtained from the acetone extract so that artifacts present in the acetone extract volatiles could be recognized.

**Gas Chromatography.** Chromatographic separations were carried out with Hewlett-Packard 5830 gas chromatographs fitted with flame ionization detectors. DB-1 and DB-wax 60 m  $\times$  0.32 mm fused silica columns were employed. Operating conditions for the DB-1 column were as follows: head pressure, 14 psi; temperature program,  $50^{\circ}\text{C}$  for 0.1 min,  $50\text{--}250^{\circ}\text{C}$  at  $4^{\circ}\text{C}/\text{min}$ , and then  $250^{\circ}\text{C}$  for 5 min. This column was used for most of the GC/MS identification work and Kovats index determinations. For the DB-wax column, operating conditions were as follows: head pressure, 21.8 psi; temperature program,  $50^{\circ}\text{C}$  for 0.1 min,  $50\text{--}230^{\circ}\text{C}$  at  $4^{\circ}\text{C}/\text{min}$ , and then  $230^{\circ}\text{C}$  for 10 min. Measured amounts of undecane (about  $4\ \mu\text{g}$  of undecane/g of melons or vines) were added to concentrates of volatiles in order to calculate yields.

**Component Identification.** Identifications were based on mass spectral data obtained with a Finnegan MAT 4500 gas chromatograph/mass spectrometer/data system and were verified by Kovats index comparisons on the DB-1 column or DB-wax column.

**Synthesis of *cis*-Sabinol.** *trans*-Sabinol acetate, obtained from oil of savin by distillation and silica gel chromatography, was saponified to give *trans*-sabinol. Oxidation of *trans*-sabinol in dichloromethane by pyridinium chlorochromate in the presence of sodium acetate

(Corey and Suggs, 1975) gave 4-methylene-1-(1-methyl-ethyl)bicyclo[3.1.0]hexan-3-one in 30% yield after purification by chromatography on silica gel. Reduction of this ketone by sodium borohydride in methanol afforded both *cis*- and *trans*-sabinol. Preparative GC was used to isolate *cis*-sabinol. H NMR ( $\text{CDCl}_3$ ):  $\delta$  2.27 ( $\text{C}_{2\alpha}\text{-H}$ ,  $J_{2\alpha,2\beta} = 12.3$ ,  $J_{2\alpha,3} = 7.3$ ,  $J_{2\alpha,10a} = 0.5$ ), 1.59 ( $\text{C}_{2\beta}\text{-H}$ ,  $J_{2\beta,3} = 8.0$ ,  $J_{2\beta,6\beta} = 1.5$ ), 4.20 ( $\text{C}_3\text{-H}$ ,  $J_{3,6\beta} = 1.5$ ,  $J_{3,10a} = 2.3$ ,  $J_{3,10b} = 2.0$ ), 1.70 ( $\text{C}_5\text{-H}$ ,  $J_{5,6\alpha} = 4.0$ ,  $J_{5,6\beta} = 8.5$ ), 0.57 ( $\text{C}_{6\alpha}\text{-H}$ ,  $J_{6\alpha,6\beta} = 5.0$ ), 0.65 ( $\text{C}_{6\beta}\text{-H}$ ), 1.39 ( $\text{C}_7\text{-H}$ ,  $J_{7,8} = J_{7,9} = 7.0$ ), 0.95 ( $\text{C}_8\text{-H}$ ), 0.89 ( $\text{C}_9\text{-H}$ ), 4.99 ( $\text{C}_{10a}\text{-H}$ ,  $J_{10a,10b} = 8.8$ ), 4.87 ( $\text{C}_{10b}\text{-H}$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  33.4 ( $\text{C}_1$ ), 37.5 ( $\text{C}_2$ ), 71.4 ( $\text{C}_3$ ), 156.1 ( $\text{C}_4$ ), 27.8 ( $\text{C}_5$ ), 17.8 ( $\text{C}_6$ ), 33.0 ( $\text{C}_7$ ), 19.5 ( $\text{C}_8$  or  $\text{C}_9$ ), 19.6 ( $\text{C}_8$  or  $\text{C}_9$ ), 102.0 ( $\text{C}_{10}$ ). Proton spectra were obtained at 200 MHz and  $^{13}\text{C}$  spectra at 50 MHz on a Nicolet WB200 equipped with a Nicolet 1280 computer and a 293B pulse programmer. Carbon multiplicities were determined with use of the APT pulse sequence supplied with the Nicolet software.

#### RESULTS AND DISCUSSION

Table I lists the volatile compounds identified in bittermelons and bittermelon vines, the quantities found, and the experimental and reference retention indices of the compounds on the DB-1 and DB-wax columns. Each compound listed was identified by its mass spectrum obtained during a GC/MS run. Of the 50 compounds, 27 are alcohols, 15 aldehydes, 2 ketones, 3 esters, and 2 hydrocarbons and 1 is an acid. About half were not found in volatiles of the closely related plants cucumber, honeydew melon, muskmelon, squash, and watermelon.

Not included in Table I are several ketonic compounds adjudged to be artifacts. Prominent among these are diacetone alcohol and 4-methylpent-3-en-2-one. Volatiles obtained from an acetone extract were compared to those from an ether extract or to compounds recovered from freeze-dryer ice. However, use of acetone for extraction has the merits of minimizing the enzymatic production of aldehydes that occurs upon blending with water and of recovering water-soluble compounds more efficiently than by use of steam distillation and extraction in a Likens and Nickerson apparatus.

The presence of myrtenol is of major interest. Myrtenol has been identified in species of at least 11 other plant families but to our knowledge never before in a Cucurbitaceae species. It also seems that in none of the investigated species does myrtenol constitute as large a part of the volatiles as it does in bittermelon.

*cis*-Sabinol is shown to be a naturally occurring compound and present in bittermelon. A peak in the DB-1 gas chromatogram with KI 1147 gave a good MS match for sabinol but was not the common *trans*-sabinol which has KI 1122. *cis*-Sabinol was synthesized and proved to have the same retention time and mass spectrum as the unknown compound. Although *cis*-sabinol was previously unknown as a natural compound, there is a report of 0.1% *cis*-sabinyl acetate in the essential oil of *Artemisia absinthium* L. (Vostrowsky et al., 1981). This essential oil also contained 3.2% *trans*-sabinol and 27.8% *trans*-sabinol acetate. There is no evidence of these two compounds in bittermelon.

In that the qualitative composition of volatile compounds in melons and vines is very similar, it is likely that both plant parts contribute to the attractancy. Their odors seem the same, and their cumulative emanations would send a strong signal to the melon fly. Initial tests of attractancy of bittermelon volatiles for the melon fly show that volatiles obtained from the acetone extract by steam distillation are strongly attractive. Further tests will be carried out to determine which compound or mixture of

**Table I. Volatile Components of Bittermelons and Bittermelon Vines**

	yield, ppm		KI, <sup>a</sup>			
	melon	vine	KI, DB-1		DB-wax	
			exptl	ref	exptl	ref
propan-2-ol	0.02	0.06		475	917	921
propan-1-ol		0.14		534	1030	1031
acetic acid	b	b		580	1451	1450
ethyl acetate <sup>d,e</sup>	b	b	600	600	877	882
2-methylpropanol	0.07	0.27	608	608	1084	1084
trans-but-2-enal		0.02		622	1034	1035
butanol <sup>e,f</sup>	0.06	0.07	637	638	1137	1139
benzene	0.01	0.01	642	644	938	937
pent-1-en-3-one	0.02	0.08		658	1016	1018
pent-1-en-3-ol <sup>g</sup>	0.46	0.91	659	658	1150	1155
pentanal <sup>f</sup>	0.09	0.05		668	973	973
pentan-3-ol		0.02		669	1104	1104
pentan-2-ol	0.01	0.01		677	1116	1116
3-methylbut-3-enol	0.01	0.08	710	711	1242	1245
3-methylbutanol <sup>f</sup>	0.06	0.21	714	714	1203	1205
trans-2-methylbut-2-enal		0.01		715	1090	1092
2-methylbutanol <sup>e</sup>	0.04	0.07	718	718	1201	1203
trans-pent-2-enal <sup>f</sup>	0.06	0.13		723	1124	1123
pentanol <sup>e,f</sup>	0.05	0.13	744	744	1245	1250
trans-pent-2-en-1-ol	0.06	0.04		744	1307	1309
cis-pent-2-en-1-ol <sup>f</sup>	0.70	0.66	747	746	1314	1317
hexanal <sup>c,f,g</sup>	0.10	0.06		772	1077	1078
2-methylpent-2-enal		0.13	804	808	1151	1155
trans-hex-2-enal <sup>c,f,g</sup>	0.17	0.30	823	823	1214	1215
trans-hex-3-enol <sup>f</sup>	0.02	0.05	830	830	1363	1362
cis-hex-3-enol <sup>c,g</sup>	0.93	4.85	834	834	1377	1378
cis-hex-3-enyl formate		0.01		836	1261	1260
trans-hex-2-enol <sup>g</sup>		0.04	846	844	1401	1404
hexanol <sup>c,g</sup>	0.19	0.13	849	848	1349	1352
trans,trans-hexa-2,4-dienal	0.01	0.01		876	1395	1397
benzaldehyde <sup>d,g</sup>	0.01	0.12	926	926	1511	1516
heptanol	0.02	0.02		951	1456	1455
trans,trans-hepta-2,4-dienal <sup>f</sup>	0.06	0.07		979	1485	1486
cis-hex-3-enyl acetate <sup>d,e</sup>		0.04	986	985	1311	1315
benzyl alcohol <sup>h</sup>	0.20	1.10	1005	1004	1869	1872
phenylacetaldehyde <sup>g</sup>	0.07	0.12	1007	1006	1631	1636
p-cymene		0.02		1011	1264	1268
octanol <sup>e,f</sup>	0.01	0.01		1053	1554	1557
2-phenylethanol <sup>f</sup>	0.02	0.11	1082	1081	1901	1908
nonanal <sup>c,g</sup>		0.02	1081	1082	1389	1389
linalool		0.01		1083	1542	1545
cis-verbenol		0.03		1122	1652	1652
cis-sabinol	0.02	0.20	1147	1147	1783	1782
4-terpineol		0.03		1159	1598	1600
myrtenal	0.04	0.15	1167	1166	1622	1624
myrtenol	0.81	8.65	1177	1177	1788	1791
nonadienal isomer <sup>c,f</sup>	0.03				1657	
trans,trans-nona-2,4-dienal	0.23		1185	1184	1693	1697
$\beta$ -ionone <sup>c,g</sup>		0.06		1462	1935	1936
nerolidol <sup>g</sup>	0.02			1547	2034	2037

<sup>a</sup> Experimental and reference Kovats indices. <sup>b</sup> Yield not given because much would have been lost in processing. <sup>c</sup> Found in cucumber. <sup>d</sup> Found in honeydew melon. <sup>e</sup> Found in muskmelon. <sup>f</sup> Found in watermelon. <sup>g</sup> Found in squash blossoms.

compounds provides this effect.

#### ACKNOWLEDGMENT

We thank Mabry Benson for obtaining NMR spectra and Roy Cunningham for testing bittermelon volatiles as an attractant for the melon fly.

**Registry No.** 2-Propanol, 67-63-0; 1-propanol, 71-23-8; acetic acid, 64-19-7; ethyl acetate, 141-78-6; 2-methylpropanol, 78-83-1; trans-2-butenal, 123-73-9; 1-butanol, 71-36-3; benzene, 71-43-2;

1-penten-3-one, 1629-58-9; 1-penten-3-ol, 616-25-1; pentanal, 110-62-3; 3-pentanol, 584-02-1; 2-pentanol, 6032-29-7; 3-methyl-3-butenol, 763-32-6; 3-methylbutanol, 123-51-3; trans-2-methyl-2-butenal, 497-03-0; 2-methylbutanol, 137-32-6; trans-2-pentenal, 1576-87-0; pentanol, 71-41-0; trans-2-penten-1-ol, 1576-96-1; cis-2-penten-1-ol, 1576-95-0; hexanal, 66-25-1; 2-methyl-2-pentenal, 623-36-9; trans-2-hexenal, 6728-26-3; trans-3-hexenal, 928-97-2; cis-3-hexenal, 928-96-1; cis-3-hexenyl formate, 33467-73-1; trans-2-hexenal, 928-95-0; hexanol, 111-27-3; trans,trans-hepta-2,4-dienal, 4313-03-5; cis-3-hexenyl acetate, 3681-71-8; benzyl alcohol, 100-51-6; phenylacetaldehyde, 122-78-1; p-cymene, 99-87-6; octanol, 111-87-5; 2-phenylethanol, 60-12-8; nonanol, 124-19-6; linalool, 78-70-6; cis-verbenol, 1845-30-3; cis-sabinol, 471-16-9; 4-terpineol, 562-74-3; myrtenal, 564-94-3; myrtenol, 515-00-4; nonadienal, 30551-17-8; trans,trans-nona-2,4-dienal, 5910-87-2;  $\beta$ -ionone, 79-77-6; nerolidol, 142-50-7; trans-sabinol acetate, 53833-85-5; trans-sabinol, 29606-76-6; 4-methylene-1-(1-methylethyl)bicyclo[3.1.0]hexan-3-one, 119068-54-1.

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Received for review June 14, 1988. Accepted September 19, 1988.