

Volatile Components of Safflower

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Volatile components of safflower (*Carthamus tinctorius* L.) flowerhead buds, flowers, and leaves and stems were identified by gas chromatography-mass spectrometry. 1-Pentadecene is the major component of buds and leaves and stems. In flowers, the major part of the volatiles consists of a mixture of polyacetylenes. Of 86 compounds identified, 66 were not previously identified in safflower. 1,2,3-Trimethoxy-5-methylbenzene is reported in a Compositae species for the first time.

Comparisons of the volatile component profiles of thistle species are of interest to us because of efforts to introduce and establish populations of monophagous biocontrol insects for suppression of undesirable thistle species, such as yellow starthistle (*Centaurea solstitialis* L.). Host-finding and ovipositing behaviors of insects that are candidates for biological control agents may be mediated by chemical cues from the plants. Identification of the volatile chemical cues from yellow starthistle will be determined directly by bioassays with volatiles identified in yellow starthistle (Binder et al., 1990) and indirectly by comparison of composition of yellow starthistle volatiles with compositions of volatiles from nonhost thistle species including the crops artichoke (*Cynara scolymus* L.) and safflower (*Carthamus tinctorius* L.).

Previous work on identification of volatile safflower compounds focused on polyacetylenes. From roots and aerial parts, a total of nine C₁₃ and one C₁₄ polyacetylenes was found (Bohlmann et al., 1966). These were hydrocarbons, epoxides, alcohols, acetate esters, and chlorohydrins. Upon further investigation, another C₁₃ polyacetylene epoxide and three isovalerate esters of C₁₀ polyacetylene alcohols were also found (Bohlmann and Zdero, 1970). When safflower was infected with *Phytophthora drechsleri*, strong antifungal activity was provided by (*E,E*)-3,11-tridecadiene-5,7,9-triylne-1,2-diol and its dehydro derivative (*E*)-11-tridecene-3,5,7,9-tetraene-1,2-diol (Thomas and Allen, 1970; Allen and Thomas, 1971). Three of the polyacetylenic C₁₃ hydrocarbons found by Bohlmann et al. (1966) and three others not previously identified were isolated from immature safflower seeds (Ichihara and Noda, 1975). The distribution and metabolism of these six compounds and an epoxide were determined in seedlings and 120-day-old plants (Ichihara and Noda, 1977).

Safflower flowers yielded two nematocidal polyacetylenes (Kogiso et al., 1976). Germination of *Puccinia carthami* teliospores was stimulated by safflower polyacetylenes (Binder et al., 1977); 10 active compounds were identified (Binder et al., 1978).

Some 1-alkenes have been found in safflower seedlings. Binder et al. (1975) identified (*Z,Z,Z*)-1,8,11,14-heptadecatetraene, previously found only in the roots of *Saussurea lappa*, another member of the tribe Cynareae. In a study of the biosynthesis of 1-alkenes in higher plants, this compound, its dihydro and tetrahydro derivatives, 1-pentadecene, and 1-heptadecene were the predominant hydrocarbons in germinating safflower (Ney and Boland, 1987).

EXPERIMENTAL PROCEDURES

Materials. In June 1987, safflower plants were collected from a field of experimental variety 555 (Seedtec International) near Woodland, CA. Two samples were prepared from these plants: flowerhead buds and a combination of leaves and stems. In June 1989, flowerheads were collected from a field of experimental variety 3033 (Seedtec International) near Woodland. To obtain the flower samples, a razor cut was made across the base of each flowerhead and the involucre was separated and discarded.

Isolation of Volatiles. Flowerhead buds (1000 g) were blended with distilled acetone in a Waring Blendor. The mixture was filtered, and the filter cake was rinsed with acetone before being reblended with acetone and filtered. The filter cake was then suspended in ether, filtered, resuspended in hexane, and filtered. Solvent was removed from the acetone extract by distillation under reduced pressure, and the distillate comprising acetone plus some volatile plant components was collected in a chilled flask.

Solvent was distilled from the ether and hexane extracts at atmospheric pressure, and pot residues were added to the residues from distillation of acetone. Distilled water was added, and vacuum steam distillation was conducted for 4 h. Distillation of the previously collected acetone distillate through a packed column at atmospheric pressure removed most of the acetone, leaving a watery solution of safflower volatiles which was added to the steam distillate. The mixture was saturated with salt and extracted with ether. The ether solution was dried with anhydrous sodium sulfate and concentrated to 2 mL by distillation of ether. In similar fashion, a concentrate of volatiles was obtained from 1000 g of stems and leaves. In obtaining volatiles from 486 g of flowers, ether was used only for extraction from the steam distillate.

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 × 0.32 mm fused silica columns (J&W Scientific) were employed. Operating conditions for the DB-1 column were as follows: head pressure, 24 psi; temperature program, 50–230 °C at 4 °C/min and then 230 °C for 10 min. Operating conditions for the DB-Wax column were the same except head pressure was 21.5 psi. A measured amount of dodecane was added to an aliquot of a volatiles concentrate to calculate yields. Correction for detector response was not attempted.

Component Identification. Identifications were based on mass spectral data obtained with a Finnigan MAT 4500 gas chromatograph/mass spectrometer/data system and were verified by Kovats index comparisons on the DB-1 or DB-Wax column. ¹H NMR (200 MHz) spectra were obtained for CDCl₃ solutions with TMS as internal standard.

Liquid Chromatography. Identification of safflower flower volatiles was facilitated by chromatography of a sample on a 25 mm × 95 cm column of silica gel 60H in hexane and subse-

Table I. Volatile Components of Safflower

compound	concn, $\mu\text{g/g}$			Kovats index		compound	concn, $\mu\text{g/g}$			Kovats index	
	buds	flowers	leaves/ stems	DB-1	DB-Wax		buds	flowers	leaves/ stems	DB-1	BD-Wax
ethyl acetate	0.14	0.04		600	882	alloaromadendrene	0.01			1455	1642
2-methylpropanol	0.07			608	1084	β -ionone	0.07	0.88	0.09	1462	1936
benzene	0.13	0.25		644	937	γ -muurolene	0.06			1469	1683
pent-1-en-3-ol	0.31	0.07	0.11	658	1149	germacrene D			0.04	1473	1704
pentanal			0.04	668	975	β -selinene	0.14	0.29	0.11	1480	1715
pent-3-en-2-one	0.28		0.07	711	1120	dihydroactinidiolide	0.02	0.10		1483	2348
(<i>E</i>)-2-methyl-2-butenal	0.05			715	1092	1-pentadecene ^a	110.30	8.95	137.50	1489	1545
(<i>E</i>)-2-pentenal	0.07			723	1123	α -muurolene	0.09			1492	1719
pentanol	0.13			744	1247	δ -cadinene	0.84	0.63	0.12	1513	1752
(<i>E</i>)-2-pentenol	0.01		0.10	744	1309	(<i>Z</i>)-3-hexenyl benzoate	0.04		0.05	1542	2118
(<i>Z</i>)-2-pentenol	0.23			746	1317	polyacetylene (MW 168)	0.14	0.13	0.02	1547	
hexanal	0.06			772	1075	caryophyllene epoxide	2.39	4.54	1.14	1567	1982
3-hexanol		0.10		776	1192	1-hexadecene ^a	0.11	0.05	0.22	1586	1644
2-hexanol		0.12		780	1216	(<i>E,Z,E</i>)-1,3,5,11-trideca- tetraene-7,9-diyne ^a	1.91	27.70	3.04	1597	2310
2-methylpent-2-enal	0.20			808	1155	1,3,5,11-tridecatetraene- 7,9-diyne isomer					
(<i>E</i>)-2-hexenal	0.53	0.60	1.67	822	1212	unknown	0.03	0.89	0.08	1616	2290
3-methylbutyric acid		1.20		830		(<i>Z,Z</i>)-1,3,11-tridecatriene- 5,7,9-triyne ^a		0.82		1618	2305
(<i>Z</i>)-3-hexenol	0.57		1.41	834	1378	unknown	0.14	3.09	0.28	1619	2295
2-methylbutyric acid		0.11		842		1,3,5,11-tridecatetraene- 7,9-diyne isomer	0.08	0.15	0.14	1640	2366
(<i>E</i>)-2-hexenol	0.22		0.73	844	1404	(<i>E,E,E</i>)-1,3,5,11-trideca- tetraene-7,9-diyne ^a	2.81	48.24	3.52	1648	2405
ethylbenzene	0.05	0.04		844	1124	(<i>Z,E,E</i>)-1,3,5,11-trideca- tetraene-7,9-diyne ^a	0.31	12.93	0.80	1652	2375
hexanol	0.27		1.06	848	1352	(<i>Z,Z</i>)-1,8,11-heptadeca- triene ^a	0.69	1.42	1.74	1655	1805
<i>m</i> -xylene	0.12			852	1138	(<i>Z,E</i>)-1,3,11-tridecatriene- 5,7,9-triyne ^a	2.60	95.00	1.50	1656	2392
<i>p</i> -xylene	0.05	0.24		853	1132	(<i>Z,Z,Z</i>)-1,8,11,14-hepta- decatetraene ^a	1.54	7.80	3.22	1657	1867
<i>o</i> -xylene	0.05	0.11		876	1182	(<i>Z</i>)-1,11-tridecadiene- 3,5,7,9-tetrayne ^a	0.20	0.32	0.09	1672	2391
benzaldehyde	0.10		0.04	926	1516	(<i>E,E</i>)-1,3,11-tridecatriene- 5,7,9-triyne ^a	1.74	10.00	1.22	1685	2462
(<i>E</i>)-2-heptenal	0.02		0.04	927	1317	(<i>E,Z</i>)-1,3,5-tridecatriene- 7,9,11-triyne		11.50		1687	
(<i>Z</i>)-2-heptenal	0.03			927	1320	1-heptadecene ^a	0.37	0.31	0.51	1690	
phenol	0.04			957	1996	(<i>E</i>)-1,11-tridecadiene- 3,5,7,9-tetrayne ^a	1.32	6.33	0.26	1710	2484
α -phellandrene	0.01		0.01	996	1160	(<i>Z</i>)-1,3-tridecadiene- 5,7,9,11-triyne	0.75	8.10	0.10	1727	
decane	0.01			1000	1000	(<i>E,E</i>)-1,3,5-tridecatriene- 7,9,11-triyne ^a	0.49	13.25	0.40	1732	2515
phenylacetaldehyde	0.10	1.22	0.07	1006	1636	(<i>E</i>)-1,3-tridecadiene- 5,7,9,11-triyne ^a	0.79	3.28	0.18	1758	
<i>p</i> -cymene	0.01		0.03	1010	1263	deca-4,6-diyn-1-yl 3-methylbutyrate ^a	0.72	12.21	0.59	1773	2406
limonene	0.01		0.01	1020	1195	1-tridecene-3,5,7,9,11- pentayne ^a	0.39	0.79	0.07	1778	
nonanal	0.07	0.03	0.13	1082	1388	(<i>Z</i>)-8-decene-4,6-diyn-1-yl 3-methylbutyrate ^a	0.86	19.67	0.51	1787	2480
terpinen-4-ol	0.01	0.10		1159	1600	(<i>E,Z</i>)-2,8-decadiene-4,6-diyn- 1-yl 3-methylbutyrate (tentative) ^a		1.09		1851	2596
(<i>Z</i>)-3-hexenyl butyrate			0.01	1167	1456						
verbeneone		0.16		1178	1704						
decanal		0.03	0.03	1184	1494						
benzothiazole		0.01	0.03	1186	1951						
β -cyclocitral	0.03		0.05	1194	1614						
hexyl 3-methylbutyrate	0.01			1226	1444						
(<i>E,E</i>)-2,4-decadienal		0.15		1287	1807						
1-tridecene	0.16		0.19	1289							
tridecene	0.02			1300	1300						
methyl cinnamate		0.08		1348	2068						
cyclosativene	0.09			1367	1479						
1,2,3-trimethoxy-5-meth- yl benzene		1.12		1368	2041						
α -copaene	0.17	0.22	0.05	1373	1489						
1-tetradecene ^a	3.10	0.08	3.66	1389							
sesquiterpene	0.02	0.30		1399							
α -gurjunene	0.04			1407	1528						
α -cedrene	0.24	1.40		1409	1565						
caryophyllene	43.52	50.00	27.60	1414	1592						
(<i>E</i>)- β -farnesene	0.05	0.19	0.04	1447	1660						
humulene	1.62	2.00	1.13	1448	1665						

^a Compound previously reported in safflower.

quent analyses of fractions. Eluting solvents were hexane and ether-hexane mixtures. Ultraviolet spectra of fractions were obtained and compared with GC chromatograms. Further resolution of mixtures was accomplished by chromatography on silica gel columns, by TLC, and by preparative GC.

RESULTS AND DISCUSSION

Table I lists the volatile compounds identified in safflower flowerhead buds, flowers, and leaves and stems, the quantities found, and the reference retention indices of the compounds on the DB-1 and DB-Wax columns. Each compound listed was identified by the correlation

of its mass spectrum obtained during a GC-MS run and the correspondence of experimental and reference retention indices. The unknowns in Table I were partially characterized, and compounds were tentatively identified when the mass spectra were strongly distinctive but no reference samples were available. Amounts of volatiles in Table I total 185.13 $\mu\text{g/g}$ buds, 362.41 $\mu\text{g/g}$ flowers, and 195.83 $\mu\text{g/g}$ stems and leaves.

The major part of the volatiles in buds and leaves and stems consists of seven 1-alkenes. Predominant among these is 1-pentadecene. This compound accounts for 60% of the volatiles of buds and 70% of volatiles of leaves

Table II. Mass Spectral Data from Polyacetylenes and Unknowns (Obtained during GC/MS Run, 70 eV)

compound	M ⁺	mass spectral data, m/z (rel intensity)
sesquiterpene (KI 1399, DB-1)	204	204 (100), 189 (67), 161 (40), 133 (30), 119 (52), 105 (56), 93 (17), 91 (46), 77 (17), 41 (24)
polyacetylene (KI 1547, DB-1)	168	168 (79), 167 (11), 166 (18), 165 (61), 153 (24), 152 (100), 139 (19), 115 (37), 90 (24), 89 (34)
(<i>E,Z,E</i>)-1,3,5,11-tridecatetraene-7,9-diyne	168	168 (36), 167 (21), 166 (14), 165 (43), 153 (35), 152 (100), 141 (13), 139 (19), 128 (14), 115 (33)
polyacetylene (KI 1607, DB-1)	168	168 (44), 167 (16), 166 (16), 165 (47), 153 (28), 152 (100), 141 (13), 128 (14), 115 (25), 77 (11)
unknown (KI 1616, DB-1)		187 (2), 159 (7), 136 (100), 109 (19), 105 (21), 93 (21), 91 (35), 79 (30), 69 (32), 41 (35)
(<i>Z,Z</i>)-1,3,11-tridecatriene-5,7,9-triyne	166	167 (9), 166 (72), 165 (100), 164 (26), 139 (28), 126 (24), 115 (11), 98 (14), 87 (14), 86 (13)
unknown (KI 1619, DB-1)		205 (1), 187 (3), 159 (8), 136 (100), 105 (22), 93 (25), 91 (37), 79 (33), 69 (35), 41 (38)
polyacetylene (KI 1640, DB-1)	168	168 (58), 167 (12), 166 (13), 165 (51), 153 (28), 152 (100), 141 (8), 139 (9), 128 (10), 115 (23)
(<i>E,E,E</i>)-1,3,5,11-tridecatetraene-7,9-diyne	168	168 (58), 167 (15), 166 (15), 165 (44), 153 (28), 152 (100), 141 (14), 139 (19), 128 (14), 115 (35)
(<i>Z,E,E</i>)-1,3,5,11-tridecatetraene-7,9-diyne	168	168 (51), 167 (16), 166 (10), 165 (34), 153 (30), 152 (100), 141 (16), 139 (16), 128 (16), 115 (38)
(<i>Z,E</i>)-1,3,11-tridecatriene-5,7,9-triyne	166	167 (7), 166 (64), 165 (100), 164 (26), 163 (13), 150 (9), 139 (26), 138 (14), 126 (21), 115 (10)
(<i>Z</i>)-1,11-tridecadiene-3,5,7,9-tetrayne	164	165 (18), 164 (100), 163 (69), 149 (2), 139 (3), 138 (38), 137 (11), 122 (6), 110 (30), 98 (17)
(<i>E,E</i>)-1,3,11-tridecatriene-5,7,9-triyne	166	167 (7), 166 (60), 165 (100), 164 (29), 163 (17), 150 (5), 139 (29), 138 (8), 126 (11), 115 (11)
(<i>E,Z</i>)-1,3,5-tridecatriene-7,9,11-triyne	166	167 (5), 166 (40), 165 (100), 164 (27), 163 (18), 150 (2), 140 (4), 139 (28), 126 (2), 115 (11)
(<i>E</i>)-1,11-tridecadiene-3,5,7,9-tetrayne	164	165 (13), 164 (100), 163 (71), 149 (1), 139 (4), 138 (34), 137 (14), 122 (13), 110 (26), 98 (18)
(<i>Z</i>)-1,3-tridecadiene-5,7,9,11-tetrayne	164	165 (12), 164 (90), 163 (100), 139 (9), 138 (78), 137 (24), 122 (13), 110 (18), 98 (18), 86 (20)
(<i>E,E</i>)-1,3,5-tridecatriene-7,9,11-triyne	166	167 (7), 166 (54), 165 (100), 164 (29), 163 (18), 150 (2), 140 (4), 139 (30), 126 (2), 115 (12)
(<i>E</i>)-1,3-tridecadiene-5,7,9,11-tetrayne	164	165 (14), 164 (98), 163 (100), 139 (9), 138 (79), 137 (25), 122 (13), 110 (20), 98 (19), 86 (21)
deca-4,6-diyn-1-yl 3-methylbutyrate	234	234 (11), 177 (36), 149 (35), 132 (100), 117 (83), 115 (62), 103 (55), 91 (80), 77 (62), 57 (61)
1-tridecene-3,5,7,9,11-pentayne	162	163 (14), 162 (100), 161 (20), 157 (4), 136 (38), 135 (16), 134 (18), 110 (42), 98 (2), 86 (13)
(<i>Z</i>)-8-decene-4,6-diyn-1-yl 3-methylbutyrate	232	232 (6), 176 (10), 147 (43), 130 (96), 128 (64), 115 (100), 103 (14), 91 (20), 77 (33), 57 (26)
(<i>E,Z</i>)-2,8-decadiene-4,6-diyn-1-yl 3-methylbutyrate	230	230 (6), 187 (16), 173 (21), 146 (20), 129 (51), 128 (34), 115 (25), 85 (68), 77 (16), 57 (100)

and stems. The concentration of 1-pentadecene in flowers is less than $1/12$ as much, and a nearly equal amount of 1,8,11,14-heptadecatetraene is present. These compounds are derived biosynthetically from palmitic and linolenic acids (Ney and Boland, 1987).

Sesquiterpenes were present at less than $1 \mu\text{g/g}$ except for caryophyllene, humulene, caryophyllene epoxide and, in flowers, α -cedrene. The concentration of caryophyllene was quite high, reaching $50 \mu\text{g/g}$ in flowers.

A complex mixture of polyacetylene hydrocarbons was present in all plant parts examined. In flowers, these compounds were at a concentration of $250 \mu\text{g/g}$ and made up 69% of the volatiles. In other plant parts, concentrations were much lower: $13.7 \mu\text{g/g}$ in buds and $11.6 \mu\text{g/g}$ in leaves and stems. All but two of the named polyacetylenes had been previously identified as safflower compounds. One of these compounds (KI 1727, DB-1) cochromatographed with (*E*)-1,3-tridecadiene-5,7,9,11-tetrayne (KI 1758, DB-1) on silica gel and displayed a mass spectrum that was nearly identical. This substance is not (*E*)- or (*Z*)-1,11-tridecadiene-3,5,7,9-tetrayne because these compounds are less polar on silica gel and have substantially different mass spectra. The compound is thus (*Z*)-1,3-tridecadiene-5,7,9,11-tetrayne. Mass spectral data for these compounds, other polyacetylenes, and unknowns are given in Table II.

Ichihara and Noda (1975) identified 1,3,5-tridecatriene-7,9,11-triyne in immature safflower seed. Comparison of

their UV data with UV data published for a tridecatrienetriyne found in the Compositae tribe Anthemideae (Bohlmann et al., 1962) convinced them that the isomer they discovered was the same as the previously described isomer which was stated to be all trans (Bohlmann and Jastrow, 1962). In our work on flower volatiles, silica gel chromatography gave a fraction containing about equal amounts of a mixture of tridecatetraenediynes and a mixture of two compounds indicated to be 1,3,5-tridecatriene-7,9,11-triynes by their mass spectra. These were separated from the tridecatetraenediynes by TLC (Ichihara and Noda, 1975). Assignment of NMR signals at δ 5.2–5.5 and 6.2–6.9 was difficult, but, with the assistance of a proton-proton correlation (COSY) and spectral simulations, it was possible to assign the *E,Z* configuration to the isomer with KI 1687. An attempt to separate the isomers was made via chromatography on a $9 \text{ mm} \times 48 \text{ cm}$ column of 1:10 AgNO_3 -silica gel. The *E,Z* isomer tended to elute sooner, but, before NMR spectra could be obtained for chromatography fractions, substantial isomerization had already occurred. At this time a paper appeared reporting that (*E,E*)- and (*E,Z*)-1,3,5-tridecatriene-7,9,11-triyne had been found among *Artemisa vulgaris* polyacetylenes and providing proton NMR data for them (Wallnofer et al., 1989). Although our data are in agreement with those of Wallnofer et al. for the *E,Z* isomer, our COSY definitely places H-4 of the other isomer at δ 6.32 rather than at δ 6.48 as they reported. We

agree that the configuration of the C-5,C-6 double bond is *E*, but our data from COSY and spectral simulations do not allow us to assign configuration at C-3,C-4.

Three 3-methylbutyrate esters of C₁₀ polyacetylene alcohols were identified. From polar fractions of safflower volatiles, two compounds with molecular weights of 232 and 234, as indicated by their mass spectra, were purified in quantity sufficient for ¹H NMR analysis. Spectral data obtained were equivalent to those given by Bohlmann and Zdero (1970) for (*Z*)-8-decen-4,6-diyn-1-yl 3-methylbutyrate and deca-4,6-diyn-1-yl 3-methylbutyrate, which they found in aerial safflower parts. They also reported (*E,Z*)-2,8-decadiene-4,6-diyn-1-yl 3-methylbutyrate, likely the compound with KI 1851 on the bases of its retention indices and mass spectrum. However, we cannot specify configurations of the double bonds. We find much higher concentrations of these compounds in flowers than in buds or leaves and stems.

An unusual compound, here reported for the first time in Compositae, was found in flowers. This compound had KI 1368 on the DB-1 column, and its mass spectrum showed the molecular ion of mass 182 as base peak along with prominent ions at *m/z* 167, 139, 124, and 109. An exact mass measurement of 182.0945 indicated the composition C₁₀H₁₄O₃ (182.0942). A sample was isolated by preparative GC on a 2% OV-17 column. In the NMR spectrum, there was a singlet at δ 2.32 (3 H, ArCH₃), a singlet at δ 3.82 (3 H, OCH₃), a singlet at δ 3.85 (6 H, OCH₃), and a singlet at δ 6.40 (2 H, Ar H). These data suggest only 2,4,6-trimethoxytoluene or 3,4,5-trimethoxytoluene. The published ¹H NMR spectrum of 2,4,6-trimethoxytoluene shows signals at δ 2.0 and 6.1, whereas the corresponding signals in the spectrum of 3,4,5-trimethoxytoluene are at δ 2.30 and 6.34 (Pouchert, 1983) so the compound in safflower flowers is the latter isomer. 3,4,5-trimethoxytoluene has been previously found in genera of Aristolochiaceae (Endo and Nakamura, 1978; Hayashi et al., 1980, 1987).

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