complexes, and bioavailability studies might necessitate seeds or other plant parts with very high specific activities, whereas other investigations such as general overall uptake and distribution studies and those determining the effect of processing on mineral concentrations would not warrant such expense. For labeling plants with either ^{51}Cr or ^{65}Zn, the higher the dose, the higher the nuclide concentration. For soybean plant parts, the highest nuclide concentration occurred when plants were continually exposed to the nuclide. For kale, plants exposed continually also accumulated the most ^{65}Zn, but nuclide concentration of ^{51}Cr was not significantly different between plants exposed only during the last 3 weeks of growth and those exposed continually. However, the exposure period and level of application that resulted in higher nuclide concentration may not result in the highest percent accumulation of an applied dose since a lower level of application may be taken up more efficiently.

The most efficient accumulation of applied dose, e.g., the most economical, for soybean seeds occurred when exposures only encompassed the reproductive phase of growth in all levels of application (Table VII). Dosing only during the reproductive period would be even more economical for ^{51}Cr than for ^{65}Zn given the short half-life of ^{51}Cr (28 days). Chromium-51 accumulation was less efficient when yields were reduced at higher levels of ^{51}Cr exposure, whereas efficiency of ^{65}Zn accumulation was similar for each level of application.

ACKNOWLEDGMENT

We gratefully acknowledge the statistical assistance so generously given by L. Weaver.

Registry No. Chromium-51, 14392-02-0; zinc-65, 13982-39-3.

LITERATURE CITED

Blincoe, C. *J. Sci. Food Agric.* **1974**, *25*, 973.
Carroll, M. D.; Loneragan, J. F. *Aust. J. Agric. Res.* **1969**, *20*, 457.
Cary, E. E.; Allaway, W. H.; Olson, O. E. *J. Agric. Food Chem.* **1977a**, *25*, 300.
Cary, E. E.; Allaway, W. H.; Olson, O. E. *J. Agric. Food Chem.* **1977b**, *25*, 305.
Epstein, E. "Mineral Nutrition of Plants: Principles and Perspectives"; Wiley: New York, 1972.
Ham, G. E.; Dowdy, R. H. *Agron. J.* **1978**, *70*, 326.
Huffman, E. W. D., Jr.; Allaway, W. H. *J. Agric. Food Chem.* **1973**, *21*, 982.
Janghorbani, M.; Weaver, C. M.; Ting, B. T. G.; Young, V. R. *J. Nutr.* **1983**, *113*, 973.
Lahouti, M.; Peterson, P. J. *J. Sci. Food Agric.* **1979**, *30*, 136.
Levine, S. E.; Weaver, C. M.; Kirleis, A. W. *J. Food Sci.* **1982**, *47*, 1283.
Luttge, U.; Higinbotham, N. "Transport in Plants"; Springer-Verlag: New York, 1979; p 17.
Lyon, G. L.; Peterson, P. J.; Brooks, R. R. *Planta* **1969**, *88*, 282.
Schmitt, H. A.; Weaver, C. M. *Proc. Indiana Acad. Sci.* **1980**, *90*, 125.
Shewry, P. R.; Peterson, P. J. *J. Exp. Bot.* **1974**, *25*, 785.
Singh, B. R.; Steenberg, K. *Plant Soil.* **1974**, *40*, 637.
Skeffington, R. A.; Shewry, P. R.; Peterson, P. J. *Planta* **1976**, *132*, 209.
Starich, G. H.; Blincoe, C. *J. Agric. Food Chem.* **1982**, *30*, 458.
Turner, M. A.; Rust, R. H. *Soil Sci. Soc. Am. Proc.* **1971**, *35*, 755.
Weiner, B. J. "Statistical Principles in Experimental Design", 2nd ed.; McGraw-Hill: New York, 1971; p 399.

Received for review April 13, 1983. Revised manuscript received November 15, 1983. Accepted Janurary 17, 1984. Journal Paper No. 9718, Indiana Agriculatural Experiment Station, West Lafayette, IN 47907.

Isolation and Identification of Volatile Constituents of Sunflowers (*Helianthus annuus* L.)

Patrick X. Etievant,* Mona Azar, Min H. Pham-Delegue, and Claudine J. Masson

Headspace and solvent extraction techniques were used to isolate volatile components of sunflowers of different varieties. Gas chromatographic and mass spectrometric analysis of the extracts and of polar fractions isolated after chromatography on silica gel led to the detection of 84 components among which 20 terpene hydrocarbons, 9 alcohols, 3 phenols, 6 esters, and 19 oxygenated compounds were identified. Forty-seven of these volatile constituents have not been reported previously in sunflowers.

Most plants are pollinated by insects. The series of new hybrids is therefore closely linked to pollen transfer from male to female lines between two plants. The discovery of cytoplasmic male sterility (Leclercq, 1969) has provided more control over the creation of new sunflower hybrids, making it possible to improve oil yield and disease resistance. Nevertheless, field observations have shown that hybrids are difficult to produce despite apparently good parentage. These low yields could be associated with a lack of pollination due to a selective visitation of insects, in particular honeybees (Cirnu and Dumitrache, 1976; Pham-Delegue et al., 1982). As the scent of a flower is one of the prime factors attracting honeybees (von Frisch, 1967), the present work was undertaken to determine the importance of individual flower volatiles in attracting insects toward both male and female parents. While a number of workers have examined sunflower oil volatiles, only one author has studied the aroma constituents of the sunflower itself (Popescu, 1979, 1982; Popescu and Fagarasan, 1979). The aim of this work was thus to complete our knowledge on volatile components emitted by sunflower heads.

Ministere de l'Agriculture, INRA, Laboratoire de Recherches sur les Aromes, 21034 Dijon Cedex, France (P.X.E. and M.A.), and Ministere de l'agriculture, INRA, Station de Recherches sur l'Abeille et les Insectes Sociaux, La Guillonerie, 91440 Bures sur Yvette, France (M.H.P-D. and C.J.M.).

EXPERIMENTAL SECTION

Material. Flower heads were removed from the stems and stored at −25 °C. All samples were analyzed within 6 months of harvest. Two batches of flower heads were examined. A bulk sample (batch A) was composed of

0021-8561/84/1432-0503$01.50/0

Table I. Chemical Composition of the Different Sunflower Extracts Isolated from Batches A and B[a]

peak no.	batch B: headspace extract, total extract	batch B: CH_2Cl_2 extract, total extract	batch B: CH_2Cl_2 extract, polar fraction	batch A, CH_2Cl_2 extract, polar fraction	M_r suggested by CI	compound identified	reliability of identification
1	traces	traces	+	+	88	acetic acid, ethyl ester	b
2	traces	0	–	+		2-methylpropanal	c
3	0	0	–	–		3-methylbutanal	c
4	12	0	–	–		2-methylbutanal	c
5	2	0	–	–		1-pentanol	c
6	0	traces	+	+	88	3-hydroxy-2-butanone	a
7	50	1	+	+	100	hexanal	a
8	2	0	–	–		2-butenoic acid, 3-methyl-, methyl ester	c
9	5	0	–	+		2-hexenal (trans)	c
10	5	0	–	–		1-hexanol	c
11	0	0	+	–		2-pentanone	c
12	32	21	–	–	136	bicyclo[3.1.0]hex-2-ene, 2-methyl-5-(1-methylethyl)- (α-thujene)	b
13	509	1000	–	–	136	bicyclo[3.1.1]hept-2-ene, 2,6,6-trimethyl- (α-pinene)	a
14	2	5	–	–	136	bicyclo[2.2.1]heptane, 2,2-dimethyl-3-methylene- (camphene)	a
15	1000	134	–	–	136	bicyclo[3.1.0]hexane, 4-methylene-1-(1-methylethyl)- (sabinene)	b
16	341	31	–	–	136	bicyclo[3.1.1]heptane, 2-methylene-6,6-dimethyl- (β-pinene)	a
17	11	traces	–	–	136	1,6-octadiene, 7-methyl-3-methylene- (myrcene)	b
18	2	traces	–	–	136	1,3-cyclohexadiene, 2-methyl-5-(1-methylethyl)- (α-phellandrene)	a
19	12	2	–	–	136	1,3-cyclohexadiene, 1-methyl-4-(1-methylethyl)- (α-terpinene)	a
20	5	traces	–	–	134	benzene, 1-methyl-4-(1-methylethyl)- (p-cymene)	b
21	236	13	+	–	136	cyclohexene, 1-methyl-4-(1-methylethenyl)- (limonene)	a
22	0	2	+	+	154	2-oxabicyclo[2.2.2]octane, 1,3,3-trimethyl- (1,8-cineole or eucalyptol)	a
23	23	10	–	–	136	bicyclo[4.1.0]heptene, 4,7,7-trimethyl- (4-carene)	b
24	0	0	+	+	120	phenylacetaldehyde	a
25	2	5	+	+	154	unknown: 43 (100), 41 (46), 71 (46), 93 (31), 39 (23), 27 (22), 81 (20), 55 (19), 111 (19), 69 (15)	
26	0	0	+	+	152	unknown: 97 (100), 43 (74), 95 (73), 81 (69), 109 (65), 53 (43), 41 (41), 56 (28), 39 (22), 27 (20)	
27	2	2	–	–	136	2,4,6-octatriene, 2,6-dimethyl- (alloocimene)	b
28	traces	1	–	–	154	unknown: 43 (100), 93 (54), 41 (50), 71 (42), 39 (32), 81 (27), 79 (24), 25 (24), 91 (21), 55 (21)	
29	0	traces	+	+	152	unknown: 34 (100), 41 (79), 39 (55), 67 (50), 27 (40), 93 (35), 83 (30), 55 (30), 109 (30), 71 (25)	

Table I (*Continued*)

peak no.	batch B: headspace extract, total extract	batch B: CH_2Cl_2 extract, total extract	batch B: CH_2Cl_2 extract, polar fraction	batch A, CH_2Cl_2 extract, polar fraction	M_r suggested by CI	compound identified	reliability of identification
30	0	1	+	+	152	unknown: 43 (100), 41 (51), 39 (36), 91 (27), 109 (29), 27 (25), 69 (24), 82 (23), 67 (18), 55 (16)	
31	44	2	–	–	150	1,7-octadien-3-one, 2-methyl-6-methylene-	b
32	2	2	+	+	152	3-cyclopentene-1-acetaldehyde, 2,2,3-trimethyl- (campholenal)	a
33	1	2	+	+	152	bicyclo[3.1.0]hexan-3-ol, 4-methylene-1-(1-methylethyl)- (sabinol)	b
34	5	2	+	+	134 or 152	unknown: 41 (100), 39 (82), 91 (75), 109 (65), 43 (58), 94 (49), 27 (38), 81 (37), 95 (30), 77 (25)	
35	0	2	–	–		unknown: 43 (100), 41 (47), 81 (34), 93 (33), 71 (32), 58 (30), 167 (26), 29 (23), 27 (22), 86 (21)	
36	2	1	+	+	150 or 168	unknown: 53 (100), 41 (98), 81 (77), 39 (62), 108 (62), 27 (42), 107 (36), 79 (35), 43 (18), 77 (18)	
37	0	2	+	–	154	bicyclo[2.2.1]heptan-2-ol, 1,7,7-trimethyl-, *endo*- (borneol)	a
38	2	1	+	+	154	3-cyclohexen-1-ol, 4-methyl-1-(1-methylethyl)- (1-terpinen-4-ol)	b
39	0	traces	+	+	150	benzenemethanol-4-(1-methylethyl)- (cumic alcohol)	b
40	0	traces	+	+	154	3-cyclohexene-1-methanol, α,α,4-trimethyl- (α-terpineol)	a
41	2	1	+	+	150	bicyclo[3.1.1]hept-2-ene-2-carboxaldehyde, 6,6-dimethyl- (myrtenal)	b
42	traces	0	–	–		bicyclo[3.1.1]heptan-3-one, 2,6,6-trimethyl- (isopinocamphone or *cis*-3-pinanone)	c
43	2	2	+	+	150	bicyclo[3.1.1]hept-3-en-2-one, 4,6,6-trimethyl- (verbenone)	a
44	0	0	+	+	152	2-cyclohexen-1-ol, 2-methyl-5-(1-methylethenyl)-, *trans*- (*trans*-carveol)	a
45	0	7	–	–		unknown: 93 (100), 91 (46), 41 (42), 121 (40), 77 (32), 39 (32), 136 (28), 27 (25), 92 (25), 43 (23)	
46	0	0	–	+	152	unknown: 43 (100), 59 (75), 94 (42), 79 (33), 67 (24), 68 (21), 41 (17), 93 (16), 95 (14), 97 (13)	
47	0	7	–	–	136	unknown: 93 (100), 41 (100), 67 (89), 68 (89), 39 (78), 27 (45), 53 (45), 79 (44), 121 (44), 94 (34)	
48	0	0	–	+	168	2,3-dioxabicyclo[2.2.2]-oct-5-ene, 1-methyl-4-(1-methylethyl)- (ascaridole)	b

Table I (*Continued*)

peak no.	batch B: headspace extract, total extract	batch B: CH_2Cl_2 extract, total extract	batch B: CH_2Cl_2 extract, polar fraction	batch A, CH_2Cl_2 extract, polar fraction	M_r suggested by CI	compound identified	reliability of identification
49	0	0	–	+	168	unknown: 83 (100), 69 (85), 43 (82), 29 (78), 55 (40), 41 (39), 71 (37), 98 (33), 97 (26), 109 (18)	
50	24	7	+	+	196	bicyclo[2.2.1]heptan-2-ol, 1,7,7-trimethyl-, acetate (bornyl acetate)	a
51	traces	1	+	+	168	unknown: 91 (100), 43 (98), 119 (66), 41 (54), 39 (44), 92 (41), 27 (24), 77 (20), 29 (16), 40 (16)	
52	2	1	+	+	194	1-cyclohexene-1-methanol, 4-(1-methylethenyl)-, acetate (perillyl acetate)	b
53	0	0	–	+	168	unknown: 43 (100), 41 (46), 97 (38), 55 (26), 71 (25), 69 (22), 82 (15), 60 (15), 39 (12), 27 (12)	
54	0	0	–	+	152	a 2,5-decadienal	b
55	0	2	+	+	180 or 196	unknown: 41 (100), 93 (89), 39 (82), 91 (55), 105 (50), 27 (48), 43 (45), 79 (40), 53 (39), 121 (38)	
56	0	1	–	–		unknown: 108 (100), 41 (57), 93 (51), 29 (37), 95 (33), 39 (29), 43 (29), 109 (29), 91 (22), 55 (18)	
57	0	traces	–	–	204	tricyclo[4.4.0.0]dec-3-ene, 1,3-dimethyl-8-(1-methylethenyl- (α-copaene)	b
58	2	2	–	–	204	cyclohexane, 1-ethenyl-1-methyl-2,4-bis(1-methylethenyl)- (β-elemene)	b
59	traces	2	–	–	204	bicyclo[7.2.0]undec-4-ene, 4,11,11-trimethyl-8-methylene- (β-caryophyllene)	b
60	0	2	–	–	204	bicyclo[3.3.1]heptane, 6-methyl-2-methylene-6-(4-methyl-3-pentenyl)-	b
61	8	15	–	–	204	1*H*-cyclopropa[*a*]-naphthalene, 1a,2,3,4,5,6,7,7a,7b-octahydro-1,1,7,7a-tetramethyl- (β-gurjunene)	b
62	0	1	–	–	204	naphthalene, decahydro-4a-methyl-1-methylene-7-(1-methylethenyl)- (β-selinene)	b
63	0	1	–	–	204	1*H*-cyclopropeazulene, decahydro-1,1,7-trimethyl-4-methylene- (aromadendrene)	b
64	2	15	–	–	204	1*H*-cyclopenta-1,3-cyclopropa-1,2-benzene, octahydro-7-methyl-3-methylene-4-(1-methylethyl)-	b
65	0	1	–	–	204	unknown: 41 (100), 93 (70), 105 (62), 107 (62), 79 (54), 91 (48), 39 (42), 67 (42), 81 (42), 108 (42)	
66	0	1	–	–	204	unknown: 41 (100), 93 (84), 107 (70), 105 (58), 29 (56), 81 (56), 39 (49), 189 (49), 79 (42), 55 (35)	

Table I (*Continued*)

peak no.	batch B: headspace extract, total extract	batch B: CH_2Cl_2 extract, total extract	batch B: CH_2Cl_2 extract, polar fraction	batch A, CH_2Cl_2 extract, polar fraction	M_r suggested by CI	compound identified	reliability of identification
67	0	traces	–	–	204	unknown: 161 (100), 41 (100), 105 (80), 91 (67), 93 (53), 79 (47), 29 (40), 119 (40), 81 (33), 27 (27)	
68	0	0	–	+	164	phenol, 2-methoxy-4-(2-propenyl)- (eugenol)	a
69	0	0	–	+	170	unknown: 59 (100), 109 (89), 43 (57), 79 (55), 41 (27), 137 (22), 108 (22), 95 (19), 69 (18), 81 (18)	
70	0	0	–	+	152	benzaldehyde, 4-hydroxy-3-methoxy- (vanillin)	a
71	0	0	–	+	186	decanoic acid, methyl ester (methyl caprate)	b
72	0	0	–	+		pentyl benzoate	c
73	0	0	–	+		5,9-undecadien-2-one, 6,10-dimethyl- (geranylacetone)	c
74	0	0	–	+		unknown: 81 (100), 29 (71), 79 (42), 41 (27), 39 (19), 77 (19), 53 (18), 163 (15), 59 (12), 55 (7)	
75	0	0	–	+	208	2,6,10,10-tetramethyl-1-oxaspiro[4.5]dec-2-en-8-one (8,9-dehydro-4,5-dihydrotheaspirone)	b
76	0	0	–	+		2-tridecanone	c
77	0	5	+	+	220	1-naphthalenol, 1,2,3,4,4a,-7,8,8a-octahydro-1,6-dimethyl-4-(1-methylethyl)- (δ-cadinol)	b
78	0	0	–	+	220	unknown: 67 (100), 81 (89), 55 (84), 41 (75), 79 (60), 95 (60), 93 (59), 43 (50), 68 (44), 69 (44)	
79	0	0	–	+	220	unknown: 43 (100), 41 (78), 123 (75), 69 (62), 93 (52), 109 (51), 91 (49), 55 (47), 81 (43), 105 (40)	
80	0	0	–	+	180	1-propanone, 1-(4-hydroxy-3-methoxyphenyl)- (propiovanillone)	a
81	0	0	–	+	220	unknown: 109 (100), 43 (96), 95 (88), 41 (85), 55 (73), 81 (68), 161 (66), 93 (64), 105 (64), 67 (64)	
82	0	0	–	+	220	unknown: 131 (100), 159 (71), 105 (63), 91 (55), 145 (49), 117 (44), 146 (31), 43 (31), 120 (30), 77 (25)	
83	0	0	–	+	218	unknown: 187 (100), 43 (64), 91 (47), 41 (45), 79 (37), 137 (36), 77 (32), 55 (31), 93 (20), 39 (20)	
84	0	0	–	+	220	unknown: 187 (100), 137 (43), 43 (30), 144 (16), 194 (15), 188 (13), 202 (11), 91 (10), 115 (9), 119 (8)	

[a] Reliability of identification. The following symbols are used: a = electronic impact (EI) mass spectrum in agreement with spectra found in the literature, confirmed by chemical ionization (CI), and Kovats indices differ by no more than 0.5% from that of the standard estimated on the same column; b = EI mass spectrum in agreement with spectra found in literature, confirmed by CI; c = EI mass spectrum in agreement with spectra found in literature. Quantitative data: the value 1000 is attributed to the area of the major peak and those of others are expressed in relation to this.

flower heads from the cultivars H_9P_2, US 894, Mariane, and Mirasol in order to provide general information on sunflower aroma constituents. Extracts and headspace collection from a single cultivar H_9P_1 (batch B) known to be poorly visited by insects were also examined and compared with those of the former.

Purification of Reagents. Solvents were carefully distilled and their purity was checked by gas chromatography (GC) as previously described (Etievant and Bayonove, 1983). Porapak Q (80–100 mesh, Waters Associates, Inc.) was extracted by using a Soxhlet extractor, first with purified methanol and then with dichloromethane for 24 h. Finally it was further purified by heating to 200 °C in a stream of nitrogen for 48 h (Williams et al., 1978).

Headspace Extraction. One frozen sunflower head was packed and allowed to thaw inside a 1-L glass reactor (Sovirel) thermostated at 30 °C and purged with nitrogen. Nitrogen (80 mL/min) purified by passage through charcoal was swept through this vessel for 36 h and the emerging gas stream passed successively through two glass tubes (7 cm × 1 cm) containing Porapak Q (1 g) onto which volatiles were adsorbed. Dry nitrogen (80 mL/min, 2 h) was then passed through the traps in the same direction as when collecting volatiles to remove excess moisture. The volatiles themselves were recovered from the traps by eluting with purified Freon 11 (50 mL). The combined solutions were concentrated to 350 μL by means of a Dufton fractionating column, sealed in glass tubes, and stored at −18 °C until examined.

Solvent Extraction. Ten frozen flower heads were placed in a Soxhlet extractor and immediately extracted for 24 h with dichloromethane (1.5 L). The resultant extract was dried over anhydrous sodium sulfate and concentrated to approximately 70 mL through a Dufton glass fractionating column. Volatile constituents were removed from the resultant concentrate by a high-vacuum cold finger distillation using the apparatus described by Forss and Holloway (1967). The distillation was allowed to continue for 8 h with the pressure ranging from 1 torr at the beginning to 5×10^{-5} torr at the end, the temperature of the flask containing the concentrate never exceeding 50 °C. Volatile materials contained in the cold traps and condensed on the cold finger were taken up in dichloromethane and concentrated to 5 mL as described before, this solvent extract being kept at −18 °C in sealed glass tubes until analyzed.

Column Chromatography. An aliquot of the solvent extract (500 μL) was placed in a thermostated column (25 cm × 1 cm i.d.; temperature 18 °C) containing silica gel (230–400 mesh, 10 g) deactivated with 35% water. The column was eluted with purified pentane (100 mL) followed by purified ether (100 mL). Pentane (apolar) and ether (polar) fractions were collected separately, concentrated to 500 μL, and sealed in tubes stored at −18 °C until examined.

Gas Chromatography. Solvent and headspace extracts together with the polar fractions derived from column chromatography were examined by using a Girdel 300 gas chromatograph fitted with a splitless glass injector, a flame ionization detector, and an SE 52 glass W.C.O.T. capillary column (37 m × 0.4 mm i.d.; film thickness 0.6 μm). Helium was used as the carrier gas (17.1 cm/min), and the oven was programmed from 40 to 180 °C at 3 °C/min. Peak areas were calculated by using a Spectra-Physics Minigrator.

Gas Chromatography–Mass Spectrometry. Gas chromatographic peaks were identified by using a Nermag R 10/10 mass spectrometer as described previously (Etievant and Bayonove, 1983). Both electron impact (EI) and chemical ionization (CI) (using NH_3 as the reagent gas) examinations were conducted. When possible, identifications were confirmed by comparison of Kovats indices with those of authentic samples. Identifications were considered to be confirmed if Kovats indices did not differ by more than 0.5%.

RESULTS AND DISCUSSION

The components identified in the different extracts obtained from the two batches of sunflowers are reported in order of increasing retention times on SE 52 in Table I. When available, molecular weights obtained from the CI examinations are given. Eighty-four components were detected as sunflower constituents, of which 57 have been identified. For the 27 unknowns, mass spectral information in the form of their 10 major EI ions and their relative intensities are given. The reliability of identification of peaks is indicated by the appropriate code letter.

The sesquiterpene alcohols and hydrocarbons reported in Table I can only be considered as tentative identifications as authentic compounds were not available for comparisons and because mass spectra of such compounds are often very similar.

Terpene hydrocarbons accounted for more than 93% of the extracts. Besides the six terpene hydrocarbons—α- and β-pinene, camphene, limonene, *p*-cymene, and α-terpinene—already cited as sunflower constituents by Popescu (1979, 1982) and Popescu and Fagarasan (1979), 17 others are reported in this work. Among these are sabinene, the major constituent in the headspace extract, and 11 sesquiterpenes. The remainder of all extracts consisted mainly of oxygenated compounds. Of the constituents reported by the same authors, evidence was found for bornyl acetate, borneol, and 1,8-cineole, but no indication could be found of menthol, isomenthol, linalool, citral, camphor, artemisia ketone, linalyl, terpinyl, and menthyl acetates also cited in these publications. Such differences could be attributed either to the different varieties studied or the different isolation procedure adopted in the two investigations. Popescu presumably examined older varieties and extracted air-dried tubular corollas instead of whole flower heads and used steam distillation as opposed to headspace and low-boiling solvent extraction techniques as used in the current investigations.

The terpenes reported are mainly biochemical byproducts of neryl pyrophosphate via the carbocation pathway derived from α-terpineol (Banthorpe et al., 1972; Schütte, 1978; Banthorpe and Charlwood, 1980). Of particular interest is the presence of α-campholenal, which is taken to originate from camphor by the action of UV radiations.

As the aim of this investigation was to understand the mechanism by which flowers attract insects, headspace examination was chosen as a means of obtaining qualitative and semiquantitative information on the volatiles in the air surrounding the flowers. However, as it was also intended to use the volatile extracts in behavioral tests with hoeny bees, more material was required than could normally be obtained by headspace techniques. Solvent extraction using dichloromethane provided comparatively large quantities of a very aromatic oil. The results of solvent extract and headspace analysis are compared qualitatively and semiquantitatively in Table I.

Most of the reported compounds were detected both in the headspace and in solvent extracts indicating that it is improbable that any could be considered as artifacts. As the concentration of compounds is lower in the extracts obtained by headspace collection than in the solvent extract, some compounds such as eucalyptol, borneol, cumic

alcohol, and α-terpineol could not therefore be detected in the headspace extract. Important quantitative differences are that α-pinene is the major component of the solvent extract whereas sabinene is the major component in the headspace extract. Myrcene, α-terpinene, limonene, 2-methyl-6-methylene-1,7-octadien-3-one, and bornyl acetate are also relatively more abundant in the headspace extract. Finally, solvent extraction also favored the extraction of high boiling sesquiterpene hydrocarbons and alcohols.

Identifications made following examination of the polar fractions are again reported in Table I. Only three additional components, 2-pentanone, phenylacetaldehyde, and *trans*-carveol, were identified after this separation, primarily because they were masked by terpene hydrocarbons in the total extract.

Comparison of the polar fractions obtained from the two batches of flower heads showed their extracts from batch A contained more material than those from B (Table I). Borneol is the only compound detected in B but not found in the extract from A. On the other hand, 23 compounds were only identified in A. The major are eugenol, propiovanillone, perillyl acetate, a decadienal (which could be considered as an oxidation product), and 8,9-dehydro-4,5-dihydrotheaspirone previously reported in tobacco (Demole and Berthet, 1972; Shibagaki et al., 1981). The occurrence of vanillin and eugenol in the polar fraction of A is consistent with the fact that two potential precursors (i.e., chlorogenic and caffeic acids) have been reported as the main polyphenolic components of sunflower seeds (Dreher and Holm, 1983). Propiovanillone has been previously identified in wines (Dubois and Brule, 1972; Etievant, 1981), but there is no evidence that this compound could be a byproduct of synthesis or degradation of lignin. However, one of its homologues, acetovanillone, can arise from the thermal degradation of ferulic acid (Fiddler et al., 1967) but such a synthetic pathway seems most improbable in the case of sunflowers.

From examination of the two polar fractions, the volatile composition of H_9P_1 sunflower heads aroma is obviously qualitatively different from that of the mixed sunflower aroma (batch A). Such differences in volatile constituents emitted by pure varieties and moreover between the two parents of the same variety are currently under investigation.

ACKNOWLEDGMENT

We gratefully acknowledge the valuable and helpful technical support of D. Demaizieres and J. Sarris for his assistance with the MS analysis in this study.

Registry No. Acetic acid ethyl ester, 141-78-6; 2-methylpropanal, 78-84-2; 2-methylbutanal, 96-17-3; 1-pentanol, 71-41-0; 3-hydroxy-2-butanone, 513-86-0; hexanal, 66-25-1; 3-methyl-2-butenoic acid methyl ester, 924-50-5; *trans*-2-hexenal, 6728-26-3; 1-hexanol, 111-27-3; 2-pentanone, 107-87-9; α-thujene, 2867-05-2; α-pinene, 80-56-8; camphene, 3387-41-5; sabinene, 3387-41-5; β-pinene, 127-19-3; myrcene, 123-35-3; α-phellandrene, 99-83-2; α-terpinene, 99-86-5; *p*-cymene, 99-87-6; limonene, 138-86-3; 1,8-cineole, 470-82-6; 4-carene, 29050-33-7; phenylacetaldehyde, 122-78-1; alloocimene, 673-84-7; campholenal, 4501-58-0; sabinol, 471-16-9; borneol, 507-70-0; 1-terpinen-4-ol, 562-74-3; cumic alcohol, 536-60-7; α-terpineol, 98-55-5; myrtenal, 564-94-3; isopinocamphone, 18358-53-7; verbenone, 80-57-9; *trans*-carveol, 1197-07-5; ascaridole, 512-85-6; bornyl acetate, 76-49-3; perillyl acetate, 15111-96-3; α-copaene, 3856-25-5; β-elemene, 33880-83-0; β-caryophyllene, 87-44-5; 6-methyl-2-methylene-6-(4-methyl-3-pentenyl)bicyclo[3.3.1]heptane, 6895-56-3; β-gurjunene, 73464-47-8; β-selinene, 17066-67-0; aromadendrene, 489-39-4; octahydro-7-methyl-3-methylene-4-(1-methylethyl)-1*H*-cyclopenta-1,3-cyclopropa-1,2-benzene, 28673-14-5; eugenol, 97-53-0; vanillin, 121-33-5; methyl caprate, 110-42-9; pentyl benzoate, 2049-96-9; geranylacetone, 3796-70-1; 8,9-dehydro-4,5-dihydrotheaspirone, 38713-26-7; 2-tridecanone, 593-08-8; δ-cadinol, 36564-42-8; propiovanillone, 1835-14-9.

LITERATURE CITED

Banthorpe, D. V.; Charlwood, B. V. "Encyclopedia of Plant Physiology"; Bell, E. A.; Charlwood, B. V., Eds.; Springer-Verlag: Berlin, Heidelberg, and New York, 1980; New Series No. 8, pp 185–220.

Banthorpe, D. V.; Charlwood, B. V.; Francis, M. J. O. *Chem. Rev.* **1972**, *72*, 115–155.

Cirnu, I.; Dumitrache, V. *Rev. Fr. Agric.* **1976**, *July*, 332–333.

Demole, E.; Berthet, D. *Helv. Chim. Acta* **1972**, *55*, 1866–1882.

Dreher, M. L.; Holm, E. T. *J. Food Sci.* **1983**, *48*, 264–265.

Dubois, P.; Brule, G. *Ind. Aliment. Agric.* **1972**, *89*, 7–9.

Etievant, P. *J. Agric. Food Chem.* **1981**, *29*, 65–67.

Etievant, P. X.; Bayonove, C. L. *J. Sci. Food Agric.* **1983**, *34*, 393–403.

Fiddler, W.; Panker, W. E.; Wasserman, A. E.; Doerr, R. C. *J. Agric. Food Chem.* **1967**, *15*, 757–761.

Forss, D. A.; Holloway, G. L. *J. Am. Oil. Chem. Soc.* **1967**, *44*, 572–575.

Leclercq, P. *Ann. Amelior. Plant.* **1969**, *19*, 99–106.

Pham-Delegue, M. H.; Fonta, C.; Masson, C.; Bonjean, A.; Madeuf, J. L.; Etievant, P. Internal Report I.N.R.A.-Promosol, Bures sur Yvette, 1982.

Popescu, H. *Farmacia (Bucharest)* **1979**, *27*, 243–247.

Popescu, H. *Clujul Med.* **1982**, *55*, 199–204.

Popescu, H.; Fagarasan, E.; Pop, L. *Clujul Med.* **1979**, *52*, 171–176.

Schütte, H. R. *Prog. Bot.* **1978**, *40*, 126–149.

Shibagaki, M.; Shibata, S.; Kaneko, H. *Agric. Biol. Chem.* **1981**, *45*, 2911–2913.

von Frisch, K. In "The Dance Language and Orientation of Bees"; Harvard University Press: Cambridge, MA, 1967.

Williams, A. A.; May, H. V.; Tucknott, O. G. *J. Sci. Food Agric.* **1978**, *29*, 1041–1054.

Received for review June 27, 1983. Revised manuscript received December 28, 1983. Accepted January 18, 1984.