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Volatile Components of *Acacia* sp. Blossoms

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Volatile component mixtures from the blossoms of three different *Acacia* sp. were examined and compared by capillary gas chromatography/mass spectrometry. Blossoms of *Acacia berlandieri* Benth. and *Acacia rigidula* Benth. are attractive to the screwworm fly *Cochliomyia hominivorax* (Coquerel), while those of *Acacia farnesiana* (L.) Willd. are inactive. A total of 114 compounds was identified in the three concentrates. Fourteen of these were found in concentrates from the two active species but could not be detected in the volatile concentrate from *A. farnesiana* blossoms. They include *trans*-5-ethenyltetrahydro-α,α,5-trimethyl-2-furanmethanol (linalool oxide A), 2-phenylethanol, *trans,cis*-2,6-nonadien-1-ol, *cis*-6-ethenyltetrahydro-2,2,6-trimethyl-2*H*-pyran-3-ol (linalool oxide D), 1-nonanol, 1*H*-indole, *trans,trans*-2,4-nonadienal, eugenol, benzyl 2-methylbutyrate, jasmone, geranylacetone, *cis*-3-hexenyl benzoate, hexyl benzoate, and benzyl salicylate.

The screwworm fly *Cochliomyia hominovorax* (Coquerel) is a serious livestock pest in the southern United States, Mexico, Central America, and South America. The female lays eggs near wounds of injured animals, and emerging maggots migrate to the wound, where they feed on living tissue, enlarging the wound and preventing healing. Mass sterile fly releases and dispersal of air-dropped baited traps are the major control strategems.

During a field study of screwworm fly behavior in southern Texas, Guillot et al. (1978) observed aggregations of screwworm flies around the blossoms of certain *Acacia* species. *Acacia berlandieri*, *Acacia rigidula*, and *Acacia greggii* shrubs contained relatively high concentrations of screwworm flies of both sexes. This was in marked contrast with that observed with *Acacia farnesiana* shrubs, which did not have any appreciable screwworm fly populations among their blossoming branches.

When blossoms of attractive species are collected, frozen for storage, and rethawed, they remain attractive to the screwworm fly (Mackley, 1978).

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The present authors initiated a comparative study of blossom volatiles from several attractive and nonattractive species of *Acacia*, in an attempt to identify those constituents responsible for the observed screwworm fly attraction.

Because of its importance in the perfume industry, *A. farnesiana* Willd. has been studied in some detail by earlier workers. The most extensive modern study was done by Demole, Enggist, and Stoll of Firminich et Cie, Geneva (Demole et al., 1969; Demole and Enggist, 1969). They used an absolute of Egyptian *A. farnesiana* blossoms as their starting material and identified 38 new constituents. Guenther (1952) has reviewed the findings of earlier studies.

EXPERIMENTAL SECTION

Starting Materials. Blossoms of *A. farnesiana* (L.) Willd., *A. berlandieri* Benth., and *A. rigidula* Benth. were collected in the Mission, TX, area in 1978 and 1981 (*A. greggii* was not available in sufficient quantity for study). The blossoms were frozen, shipped to Albany, CA, in packages containing solid carbon dioxide, and held at −30 °C until used.

Vacuum Steam Distillation/Solvent Extraction. Volatile blossom components were concentrated by using a modified Likens and Nickerson head (Flath and Forrey, 1977). Heptane (Burdick & Jackson) was used as the extracting solvent, and a system pressure of 40 mmHg was maintained during the 4-h concentration interval. Yields (based on fresh weight of blossom samples) were as follows:

Table I. *Acacia* Blossom Concentrate Constituents

component	*Acacia*[a] *ber.*	*rig.*	*far.*	KI[b]	ID MS	ID KI
methylcyclohexane			0.22	715	+	+
n-octane		0.14	0.04	800	+	+
2-heptanone		0.13		864	+	+
4-heptanol		0.10		870	+	+
3-heptanol		0.18		876	+	+
2-heptanol		0.24		881	+	+
benzaldehyde	0.01	0.34	5.98[c]	924	+	+
α-pinene	tr			928	+	+
n-propylbenzene	0.03			937	+	+
1-heptanol	0.03			951	+	+
6-methyl-5-hepten-2-one			0.18	961	+	+
1-octen-3-ol	0.06			961	+	+
β-pinene	0.02			968	+	+
6-methyl-5-hepten-2-ol	0.01			974	+	+
myrcene	0.04		1.06	982	+	+
benzyl alcohol	0.01		0.89[c]	1001	+	+
phenylacetaldehyde		1.67		1005	+	+
p-cymene	0.04			1011	+	+
2,2,6-trimethylcyclohexanone			0.07	1012	+	+
2-ethylhexanol	0.02			1013	+	+
limonene	0.07		0.20	1019	+	+
cis-ocimene			0.18	1025	+	+
trans-ocimene			0.59	1036	+	+
2-octen-1-ol	0.03			1048	+	+
1-octanol	2.04	tr	0.03	1052	+	+
linalool oxide A (*trans*-THF)	0.07	1.42		1055	+	+
methyl benzoate			0.09[c]	1064	+	+
linalool oxide B (*cis*-THF)	2.29	0.14	0.31	1069	+	+
2-phenylethanol	0.09	1.48		1080	+	+
nonanal	0.15		*c*	1081	+	+
linalool	tr	0.51	0.86	1082	+	+
n-undecane	0.01			1100	+	+
trans,cis-2,6-nonadienal	0.01	0.29	0.13	1123	+	+
benzyl acetate			0.75[c]	1128	+	+
trans-2-nonenal	0.05	0.38	0.20	1132	+	+
cis-3-nonen-1-ol	0.38	0.80	1.43	1134	+	+
trans,cis-2,6-nonadien-1-ol	0.02	0.02		1143	+	+
linalool oxide D (*cis*-THP)	0.67	0.91		1145	+	+
trans-2-nonen-1-ol	0.25	0.50	0.20	1149	+	+
linalool oxide C (*trans*-THP)	0.11			1150	+	+
1-nonanol	0.44	0.54		1153	+	+
naphthalene	0.66	0.07	2.51	1155	+	+
terpinen-4-ol	0.18			1159	+	+
methyl salicylate	0.92	1.54	94.40[c]	1164	+	+
α-terpineol	0.01			1169	+	+
myrtenol	0.55			1176	+	+
decanal		0.37	*c*	1182	+	+
benzothiazole		0.06	tr	1186	+	+
β-cyclocitral	0.02		0.37	1194	+	+
n-dodecane	0.05		0.15	1200	+	+
3-phenylpropanol	0.02			1200	+	+
p-anisaldehyde		11.06	34.36[c]	1207	+	+
nerol	0.08			1208	+	+
neral		0.75		1211	+	+
trans-cinnamaldehyde		1.28		1225	+	+
geraniol	0.14	1.85	19.45[c]	1233	+	+
geranial		0.67	5.57	1240	+	+
ethyl salicylate	0.04	0.02	0.18[c]	1243	+	+
1*H*-indole	0.04	0.42		1248	+	+
1-decanol	0.06	0.16	0.09	1255	+	+
2-methylnaphthalene	0.06	0.02	0.02	1267	+	+
trans-cinnamyl alcohol		0.66		1268	+	+
benzyl 2-methylpropionate	0.09		0.18	1269	+	+
3-methyldec-4-en-1-ol			0.92[c]	1283	+	
1-methylnaphthalene	0.02		tr	1284	+	+
trans,trans-2,4-decadienal	0.06	0.07		1286	+	+
methyl *o*-anisate		0.44		1295	+	+
n-tridecane			0.31	1300	+	+
methyl anthranilate		0.61		1301	+	+
2-methylpropyl benzoate	0.35		0.04	1302	+	+
3-methyldec-3-en-1-ol			3.83[c]	1308	+	
benzyl butyrate	0.04			1314	+	+
eugenol	1.54	2.29	*c*	1324	+	+
citronellyl acetate			0.13	1333	+	+
methyl *p*-anisate			0.31	1335	+	+
neryl acetate	0.02		0.66	1339	+	+

Table I (*Continued*)

component	*Acacia*[a] ber.	rig.	far.	KI[b]	ID MS	ID KI
methyl 2,6-dihydroxybenzoate		2.72	2.02[c]	1340	+	+
butyl benzoate	0.08			1344	+	+
benzyl 2-methylbutyrate	0.76	0.13		1357	+	+
geranyl acetate			6.56[c]	1358	+	+
jasmone	0.02	4.13		1362	+	+
benzyl 3-methylbutyrate	0.32			1364	+	+
p-anisyl acetate			0.13[c]	1376	+	+
2-methylpropyl salicylate	0.04			1398	+	+
n-tetradecane	0.09		0.22	1400	+	+
α-ionone		1.14	0.68[c]	1403	+	+
dimethyl phthalate	0.10			1406	+	+
methylbutyl benzoate[d]	0.85			1409	+	+
ethyl *p*-anisate			0.11	1410	+	+
thujopsene	0.07			1425	+	+
methyl 6-methoxysalicylate			0.59[c]	1426	+	
geranylacetone	0.05	1.65		1427	+	+
pentyl benzoate	0.06			1446	+	+
β-ionone	0.03	0.63	1.34[c]	1460	+	+
(2,6,6-trimethyl-2-hydroxycyclohexylidene)-acetic acid lactone			0.11[c]	1479	+	
n-pentadecane	0.05	0.24	0.26	1500	+	+
2-methylbutyl salicylate	0.04			1509	+	+
3-methylbutyl salicylate	0.02			1509	+	+
cis-3-hexenyl benzoate	0.26	3.60		1540	+	+
diethyl phthalate		0.24		1547	+	+
hexyl benzoate	0.12	0.22		1549	+	+
trans-2-hexenyl benzoate		0.29		1553	+	+
n-heptadecane	0.02	0.22	0.51[c]	1700	+	+
benzyl benzoate	1.02	0.36	0.09[c]	1719	+	+
n-octadecane	0.02		0.15	1800	+	+
benzyl salicylate	0.02	0.93		1824	+	+
6,10,14-trimethylpentadecanone	0.42	0.38	0.26[c]	1828	+	+
n-nonadecane	0.02	0.83	6.25[c]	1900	+	+
dibutyl phthalate	0.02	0.02	0.02	1914	+	+
n-eicosane	0.01	0.22	0.40	2000	+	+
kaur-16-ene		3.86		2031	+	
n-heneicosane	0.05	1.28	1.76	2100	+	+
n-docosane	0.02	0.06	0.09	2200	+	+
n-tricosane	0.67	0.34	0.37	2300	+	+

[a] Yield, in parts per million, from blossoms (tr = less than 5 ppb). [b] Experimentally determined Kovats Indices on the DB-1 column (conditions are in the text). [c] Compounds previously identified and/or synthesized (Demole and Enggist, 1969; Demole et al., 1969). [d] Experimental data do not distinguish between the 2-methylbutyl and the 3-methylbutyl isomers.

for *A. berlandieri*, 28 ppm (1978 blossoms) and 14 ppm (1981 blossoms); for *A. rigidula*, 74 ppm (1978); for *A. farnesiana*, 220 ppm (1981). The blossoms retained considerable aroma after the 4-h period.

Gas Chromatography. Chromatographic separations were carried out with Hewlett-Packard 5830 and 5840 gas chromatographs fitted with flame ionization detectors. Initially, large-bore stainless steel capillary columns (152 m × 0.76 mm i.d.) coated with methyl silicone oil were employed. More recent efforts have made use of 50 or 60 m long fused silica columns of 0.32-mm i.d., coated with either methyl silicone oil (OV-101) or Carbowax 20M (Hewlett-Packard) or containing either a cross-linked poly(ethylene glycol) (CP Wax 57CB; Chrompack) or a chemically bonded methyl silicone phase (DB-1; J & W Scientific). Operating conditions for the DB-1 column were as follows: head pressure = 14 psi; temperature program = 50 °C for 0.1 min, 50–250 °C at 4 °C/min, and then 250 °C for 5 min. This column was used for most of the GC/MS identification work and Kovats Index determinations.

Component Identification. Identifications were based upon unit resolution 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 60 m × 0.32 mm i.d. column.

RESULTS AND DISCUSSION

Table I summarizes the results from capillary GC/MS examination of the three blossom vacuum steam distillates. In nearly all instances, the compounds listed were identified by a combination of both mass spectral and relative retention behavior on at least one fused silica capillary column (DB-1). Authentic samples of five of the components listed in Table I were not available, so their mass spectral identifications are not supported by retention index data. However, four of these were previously identified in Demole and co-workers' *A. farnesiana* study, as were many of the *A farnesiana* components listed in the table. The last tentative identification is that of kaur-16-ene, a fairly common diterpene. Mass spectral evidence for the presence of this compound is good, and the retention index of the peak in question is consistent with such an identification, but the listing remains tentative. The three phthalate esters identified are presumably artifacts introduced during collection and storage of the blossoms.

The two esters, 2- and 3-methylbutyl salicylate, have identical retention index values on the bonded methyl silicone column. However, they were both shown to be present in the *A. berlandieri* concentrate by employing the cross-linked poly(ethylene glycol) column to resolve the two isomers in a GC/MS examination of the mixture. A

similar problem exists with 2- and 3-methylbutyl benzoate. A component peak of the *A. berlandieri* sample elutes from the DB-1 column at KI = 1409. The mass spectrum of the component peak is identical with that of both methylbutyl ester isomers. Unfortunately, both methylbutyl isomers also have identical KI values on the poly(ethylene glycol) column, so the composition of this peak cannot be fully specified.

Considerable qualitative and quantitative differences were evident among the blossom volatile concentrates from the three *Acacia* species, when examined by capillary GC/MS. The *A. berlandieri* and *A. rigidula* samples are not obviously similar, although both species are reportedly attractive in the field. The *A. farnesiana* concentrate is quantitatively quite different from the other two, and considerable qualitative differences exist as well.

If it is assumed that the blossom concentrates are representative of the respective species and that volatile components are involved in the attractive activity of *A. berlandieri* and *A. rigidula*, those compounds found in both *A. berlandieri* and *A. rigidula* but not in *A. farnesiana* are of interest. These include linalool oxide A (*trans*-tetrahydrofuranyl), 2-phenylethanol, *trans,cis*-2,6-nonadien-1-ol, linalool oxide D (*cis*-tetrahydropyranyl), 1-nonanol, 1*H*-indole, *trans,trans*-2,4-decadienal, eugenol, benzyl 2-methylbutyrate, jasmone, geranylacetone, *cis*-3-hexenyl benzoate, hexyl benzoate, and benzyl salicylate. Eugenol was reported by Demole et al. to be in Egyptian *A. farnesiana*, but it could not be detected in the Mission, TX, samples.

Quantitative results obtained from studies of biological materials are typically valid in detail only for the particular batches of samples used in the study. This holds true in the present study as well; the yield data listed in Table I hold for the concentrates prepared from specific blossom samples. However, when concentrates of other batches of *A. berlandieri* blossoms were prepared in the same manner, the concentrates differed in quantitative detail from one another, although they were qualitatively quite similar within the given species. Presumably, similar variations would have been found if additional concentrates of *A. rigidula* or *farnesiana* had been prepared.

Biological testing of the various concentrates and of blossom solvent extracts is presently under way, using screwworm flies in a four-port olfactometer system. Results of this study will be reported elsewhere.

Registry No. Linalool oxide A, 34995-77-2; 2-phenylethanol, 60-12-8; *trans,cis*-2,6-nonadien-1-ol, 28069-72-9; linalool oxide D, 14009-71-3; 1-nonanol, 143-08-8; 1*H*-indole, 120-72-9; *trans,trans*-2,4-decadienal, 25152-84-5; benzyl 2-methylbutyrate, 56423-40-6; jasmone, 488-10-8; geranylacetone, 3796-70-1; *cis*-3-hexenyl benzoate, 25152-85-6; diethyl phthalate, 84-66-2; hexyl benzoate, 6789-88-4; benzyl salicylate, 118-58-1.

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