Volatile Components of Purple Starthistle

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Volatile components of purple starthistle (*Centaurea calcitrapa* L.) flowerhead buds, flowers, leaves, and stems were identified by gas chromatography–mass spectrometry. Of the 54 compounds identified, 49 were not previously reported in purple starthistle. *cis*-Theaspirane and *trans*-theaspirane are reported for the first time in a species of Compositae. Purple starthistle and yellow starthistle (*Centaurea solstitialis* L.) volatiles are compared.

Purple starthistle (*Centaurea calcitrapa* L., Compositae) and yellow starthistle (*Centaurea solstitialis* L.) are naturalized weeds of rangelands and recreational lands in California.

Because of the economic importance of yellow starthistle in California and other states, insect natural enemies of the plant have been imported as potential biological control agents. One of these, the weevil *Bangasternus orientalis* (Capiomont), in host specificity tests with four *Centaurea* species and four species in closely related thistle tribe genera, oviposited almost exclusively on *C. solstitialis* (Maddox and Sobhian, 1987). Ovipositing on *C. calcitrapa* was about 2% as large, but no eggs were found on *Centaurea diffusa* Lam. (diffuse knapweed). The reverse situation was observed for ovipositing by *Bangasternus fausti* (Reitter), a potential biological control agent for diffuse knapweed. Many eggs were found on *C. diffusa*, about one-fourth as many on *C. calcitrapa* and none on *C. solstitialis* (Maddox and Sobhian, 1987). While looking for chemical cues for plant selection by *B. orientalis*, we have determined the volatile components of yellow starthistle (Binder et al., 1990) and purple starthistle.

Three previous reports identify some volatile compounds in purple starthistle. In an extract of roots, the polyacetylene 1,11-tridecadiene-3,5,7,9-tetrayne was detected (Bohlmann et al., 1958). Volatile oil from air-dried leaves of Egyptian purple starthistle analyzed by GC contained about 9% esters, 6% each of monoterpene hydrocarbons and ketones, 2% monoterpene alcohols, 2% miscellaneous, and 75% unidentified compounds (Karawga et al., 1975). Aerial parts contained two bisabolone derivatives and aplotaxene ((*Z*,*Z*,*Z*)-1,8,11,14-heptadecatetraene) (Jakupovic et al., 1986).

EXPERIMENTAL SECTION

Materials. Purple starthistle was collected in July 1987 from a ranch 4 miles east of Napa, CA. Three samples were prepared: closed flowerhead buds, flowers, leaves and stems. 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. Concentrates of volatiles were obtained from acetone extracts of 33 g of flowers, 504 g of leaves and stems, and 545 g of flowerhead buds essentially as previously reported for isolation of volatiles from yellow starthistle (Binder et al., 1990).

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 tetradecane was added to an aliquot of a volatiles concentrate in order 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.

RESULTS AND DISCUSSION

Table I lists the volatile compounds identified in purple starthistle buds, flowers, and leaves and stems, the quantities found, and the retention indices of the compounds on DB-1 and DB-Wax columns. Each compound listed was identified by its mass spectrum obtained during a GC–MS run. The 54 compounds identified included 11 sesquiterpenes, 10 aldehydes, 9 alcohols, 5 ketones, 5 esters, 5 aromatic hydrocarbons, 2 unsaturated and 1 saturated open-chain hydrocarbons, 2 polyacetylenes, 2 spiro ethers, and 2 sulfur-containing compounds.

Concentrations of almost all of the purple starthistle volatiles are low. Only four compounds are present in any tissue in greater than 1 μg/g concentration. Yields of volatiles were 5.5 μg/g from buds, 18.0 μg/g from flowers, and 6.1 μg/g from leaves and stems. In contrast, the corresponding yields of yellow starthistle volatiles were 31.6, 39.3, and 18.2 μg/g (Binder et al., 1990).

Of the compounds identified here in purple starthistle, 30 were also found in yellow starthistle (Table I). The major volatile in yellow starthistle was germacrene D, which is also prominent in volatiles of purple starthistle. Sesquiterpene concentrations were lower in purple starthistle except for (*E*)-α-bergamotene, (*E*)-β-farnesene in buds, and caryophyllene in flowers. Two polyacetylenes were found in flowers whereas in yellow starthistle there were 12, most being in both buds and flowers. A major difference between the plants is the relatively tiny amount of aplotaxene and 1-pentadecene in purple starthistle.

The presence of *cis*- and *trans*-theaspirane in *C. calcitrapa* buds, leaves, and stems is especially interesting. They have been reported in species of nine other plant families, but this is the first report of their presence in a species of Compositae. These compounds have substantial odors and, at the level found in purple starthistle,

Table I. Volatile Components of Purple Starthistle

compound	concentration, μg/g			Kovats index[a]	
	buds	flowers	leaves/ stems	DB-1	DB-Wax
ethyl acetate	0.09	0.82		600	882
benzene[c]	0.38	4.26	0.36	647	937
2-pentanone[c]	0.07	1.39	0.20	658	975
pent-1-en-3-ol	0.02	0.46	0.27	658	1155
3-pentanone	0.03	0.68		669	971
2-pentanol	0.03	0.45	0.02	677	1116
pent-3-en-2-one	0.32	0.10	0.02	711	1120
3-methylbutanol	0.01		0.02	714	1205
pentanol	0.06	0.08	0.03	744	1247
hydrocarbon (MW 112)	0.12	0.06	0.12	(780)	
2-methylpent-2-enal		0.40		808	1155
hex-3-en-2-one (tentative)	0.28		0.04	(813)	(1211)
(*E*)-2-hexenal[c]	0.08		1.11	822	1222
(*Z*)-3-hexenol[c]	0.18	0.12	0.56	834	1378
ethylbenzene[c]		0.18		844	1124
(*Z*)-2-hexenol			0.06	847	1413
hexanol[c]	0.02	0.04	0.14	848	1352
m-xylene		0.45	0.03	852	1138
p-xylene		0.21	0.02	853	1132
(*E*)-5-methylhex-3-en-2-one	0.06			871	1122
o-xylene		0.17	0.01	876	1182
(*E*,*E*)-2,4-hexadienal			0.22	876	1397
benzaldehyde[b,c]	0.06	0.01	0.07	926	1516
(*E*)-2-heptenal[c]			0.06	927	1320
octanal[c]		0.16		979	1285
(*E*,*E*)-2,4-heptadienal			0.02	979	1486
(*Z*)-3-hexenyl acetate	0.02		0.01	986	1310
decane		0.03		1000	1000
benzyl alcohol	0.03		0.08	1004	1864
phenylacetaldehyde[c]	0.12	0.44	0.50	1006	1636
2-phenylethanol[b,c]	0.02	0.08	0.11	1081	1902
nonanal[c]	0.02	0.16	0.05	1082	1388
methyl salicylate	0.04		0.17	1166	1772
(*Z*)-3-hexenyl butyrate[c]	0.03		0.03	1167	1459
decanal[c]	0.01	0.27	0.02	1184	1494
benzothiazole[c]	0.04		0.17	1186	1951
(*Z*)-3-hexenyl 2-methylbutyrate	0.02			1215	1472
cis-theaspirane	0.17		0.14	1290	1507
trans-theaspirane	0.14		0.11	1303	1543
α-copaene[c]	0.02		0.01	1373	1489
β-bourbonene[c]	0.03		0.01	1381	1518
caryophyllene[c]	0.55	3.09	0.11	1414	1592
(*E*)-α-bergamotene[c]	0.12	0.74	0.03	1431	1580
(*E*)-β-farnesene[c]	0.36	0.21	0.29	1447	1660
humulene[c]	0.05	0.21	0.02	1448	1665
ar-curcumene	0.11	0.07	0.01	1469	1766
germacrene D[c]	1.56	1.80	0.50	1473	1704
β-selinene[c]	0.04			1480	1715
1-pentadecene[c]	0.02		0.11	1489	1545
bicyclogermacrene[c]	0.07	0.08	0.02	1489	1733
β-bisabolene	0.09	0.13	0.01	1500	1721
(*Z*,*E*)-1,3,11-tridecatriene-5,7,9-triyne[b,c]		0.09		1656	2392
(*Z*,*Z*,*Z*)-1,8,11,14-heptadecatetraene[b,c]			0.13	1657	1867
(*E*,*E*)-1,3,11-tridecatriene-5,7,9-triyne[b,c]		0.42		1685	2462
mint sulfide[c]		0.16	0.06	1720	

[a] Experimental Kovats indices were within a few units of the listed reference indices. Indices in parentheses are experimental values observed for compounds that were not available for determination of reference index values. [b] Compound previously identified in purple starthistle. [c] Compound also present in yellow starthistle (2).

would contribute much to its odor (Winterhalter and Schreier, 1988). However, it is possible that the theaspiranes are artifacts. In quince, the theaspiranes were not original volatiles but were instead formed from the precursor 4-hydroxy-7,8-dihydro-β-ionol, especially under acidic conditions (Winterhalter and Schreier, 1988).

A judgement regarding whether differences in the volatile components of these thistles are important to host selection by *B. orientalis* must await the outcome of bioassays.

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Registry No. Ethyl acetate, 141-78-6; benzene, 71-43-2; 2-pentanone, 107-87-9; pent-1-en-3-ol, 616-25-1; 3-pentanone, 96-22-0; 2-pentanol, 6032-29-7; pent-3-en-2-one, 625-33-2; 3-methylbutanol, 123-51-3; pentanol, 71-41-0; 2-methylpent-2-enal, 623-36-9; hex-3-en-2-one, 763-93-9; (*E*)-2-hexenal, 6728-26-3; (*Z*)-3-hexenol, 928-96-1; ethylbenzene, 100-41-4; (*Z*)-2-hexenol, 928-94-9; hexanol, 111-27-3; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; (*E*)-5-methylhex-3-en-2-one, 1821-29-0; *o*-xylene, 95-47-6; (*E,E*)-2,4-hexadienal, 142-83-6; benzaldehyde, 100-52-7; (*E*)-2-heptenal, 18829-55-5; octanal, 124-13-0; (*E,E*)-2,4-heptadienal, 4313-03-5; (*Z*)-3-hexenyl acetate, 3681-71-8; decane, 124-18-5; benzyl alcohol, 100-51-6; phenylacetaldehyde, 122-78-1; 2-phenylethanol, 60-12-8; nonanal, 124-19-6; methyl salicylate, 119-36-8; (*Z*)-3-hexenyl butyrate, 16491-36-4; decanal, 112-31-2; benzothiazole, 95-16-9; (*Z*)-3-hexenyl 2-methylbutyrate, 53398-85-9; *cis*-theaspirane, 66537-40-4; *trans*-theaspirane, 66537-39-1; α-copaene, 3856-25-5; β-bourbonene, 5208-59-3; caryophyllene, 87-44-5; (*E*)-α-bergamotene, 13474-59-4; (*E*)-β-farnesene, 18794-84-8; humulene, 6753-98-6; *ar*-curcumene, 644-30-4; germacrene D, 23986-74-5; β-selinene, 17066-67-0; 1-pentadecene, 13360-61-7; bicyclogermacrene, 24703-35-3; β-bisabolene, 495-61-4; (*Z,E*)-1,3,11-tridecatriene-5,7,9-triyne, 124604-44-0; (*Z,Z,Z*)-1,8,11,14-heptadecatetraene, 10482-53-8; (*E,E*)-1,3,11-tridecatriene-5,7,9-triyne, 50739-51-0; mint sulfide, 72445-42-2.

Interrelationships between Headspace Volatile Concentration, Marketing Grades, and Flavor in Runner-Type Peanuts

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The general quality of the peanut crop within a given year is not static but is dynamic and changes in response to climatic variations and harvesting and handling variations. A quality survey of the 1987 peanut crop marketed in southwest Georgia using the headspace volatile concentration (HSVC) test indicated that sensory quality decreased and immaturity increased as the season progressed. During the first week of the marketing season, the distribution of initial-grade samples into superior, questionable, and inferior sensory quality categories as measured by the HSVC test was 86%, 10%, and 4%, respectively. The last week of the marketing season the distribution was 45%, 21%, and 34%, respectively. Taste panel intensity scoring of selected sensory attributes of roasted peanut paste made from five selected marketing grades and selected HSVC ranges indicated an inverse linear relationship between roasted peanut flavor and fruity off-flavor. There was a decrease of approximately 1 unit in roasted peanut flavor intensity for a 2-unit increase in fruity off-flavor. The data presented confirm previous suggestions that larger seed sizes are generally more flavorful and more resistant to high-temperature damage.

Curing peanuts at temperatures above 35 °C or subjecting them to freezing temperatures before they are cured may cause off-flavors in peanuts (Dickens, 1957; Singleton and Pattee, 1987a). Development of these off-flavors in peanuts is accompanied by an increase in the concentration of alcohols and aldehydes, primarily ethanol and acetaldehyde (Pattee, 1965; Singleton and Pattee, 1987a,b). The increase in concentration of these compounds is thought to result from a change in the respiration process from aerobic to anaerobic (Whitaker and Dickens, 1964; Whitaker et al., 1974). Until recently, a rapid, inexpensive, quantitative method has not been available for detecting quality deficiencies in farmers stock peanut lots (Dickens et al., 1987). The headspace volatile concentration (HSVC) test enables one to detect the presence of high-temperature off-flavor in farmers stock wagon-load lots being graded for marketing at peanut buying stations. The HSVC test was developed to be used as part of the Federal–State Inspection Service (FSIS) grading procedure. Although short-term sampling studies have been conducted (Pattee et al., 1986, 1987), a full marketing season test in which every grade sample at the peanut buying station is tested for quality has not previously been undertaken.

Previous sensory investigations by Pattee and coworkers (1986, 1989) have shown that (a) the sensory character note fruity is the appropriate sensory character note to characterize high-temperature off-flavor, (b) a relationship exists between the intensity of high-temperature off-flavor (fruity flavor) and the meter reading of the HSVC test, and (c) relationships exist between HSVC values, selected seed size ranges, and fruity flavor intensity in large-seeded virginia-type peanuts.

This study, during the 1987 crop year, was undertaken to (1) determine the variation in sensory quality, as determined by the HSVC test, across the entire mar-

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