

## VOLATILE LEAF OILS OF CALIFORNIA SALVIAS

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The *Salvia mellifera* (Labiatae) assemblage consists of *S. mellifera* Greene, *Salvia munzii* Epl., *Salvia brandegei* Epl., and *Salvia columbariae* Benth. These four species comprise a clearly defined natural group and are easily separated from the other California *Salvia* species by distinctive morphological characters. Three of these species formed subsection Parishiiella when Epling elevated two varieties within *S. mellifera* (i.e., var. *brandegei* and var. *munzii*) to specific level (1). The inclusion of the fourth member, *S. columbariae*, to the natural grouping was first suggested by Neisess (2). The most definitive characteristic of this group is the flower type, which is uniquely suited to optimize pollination by small- and medium-size bees (3). *S. mellifera* is a dominant species in much of the California coastal scrub sage and bordering chaparral zones from Contra Costa County south to the border of Baja California. In northernmost Baja California as the coastal sage scrub becomes increasingly xeric, *S. mellifera* is replaced by *S. munzii*, which ranges as far south as the vicinity of El Rosaria. *S. brandegei* occupies a narrow strip of coastline in northern Baja California, from Punta Santo Tomas south to the vicinity of Cabo Colonet and on the seaward bluffs and canyons of Santa Rosa Island off the coast of southern California. *S. columbariae*, the only annual member of this group, occurs in nearly every plant community of California from Mendocino County south and throughout much of the Sonora and Mojave Desert regions of western North America, giving it one of the widest distributions of any Californian *Salvia* species.

While previous work (2,4) was limited to the monoterpene fraction of these aromatic plants, the present paper reports on the monoterpene and sesquiterpenes of the volatile leaf oils of above species obtained by steam distillation.

The volatile leaf oil compositions are shown in Table 1.  $\beta$ -Phellandrene and 1,8-cineole could not be adequately resolved with the DB-1 column, and, therefore, separate relative values were calculated with FID, using estimations of the relative proportion of these two components determined by the single ion search capability of the ITD system.

Individual components with values falling below 0.5% are not listed in Table 1. The determination of retention times and mass spectra allows us to deduce a reasonable identification for these constituents. We list their relative retention times, identity suggested by mass spectral data and the species, *S. brandegei*, A; *S. columbariae*, B; *S. mellifera*, C; and *S. munzii*, D; where they are found, are indicated by the respective letters: 790, ethyl acetate, B; 806, allyl acetate, C; 818, 2-hexenal, B; 912, tricyclene, A,B,C,D; 916,  $\alpha$ -thujene, A,B,C,D; 959, sabinene, A,B,C,D; 984, 1-octen-3-ol, A; 1011,  $\alpha$ -terpinene, A,B,C,D; 1058, *cis*-linalool oxide, D; 1062, fenchone, A,D; 1071,  $\alpha$ -*p*-dimethyl styrene, A,B,C,D; 1077, 2-nonanone, A,D; 1084, *n*-octanol, B; 1118, *trans*-dihydrocarveol, A,B; (1134, isoborneol, D)<sup>1</sup>; 1175, *cis*-piperitol, B; 1186, *n*-decanal, B; 1187, *trans*-piperitol, D; 1187, myrtenol, D; 1187, *trans*-carveol, D; 1195, neral, A; 1214, piperitone, B; 1219, thymol methyl ether, B; 1225, geraniol, A,B,D; 1238, geranial, A,B,C; 1243, *n*-decanol, B; 1266,  $\alpha$ -cubebene, B,D; 1343, neryl acetate, D; (1346, isobornyl propionate, D); 1356, geranyl acetate, A,D; 1360,  $\alpha$ -copaene, A,B,D; 1364, *cis*-jasnone, B; 1367,  $\beta$ -bourbonene, A,B; (1373,  $\beta$ -gurjunene, B,D); 1379, isocaryophyllene, B,D; 1394,  $\alpha$ -gurjunene, B,D; (1406, alloxadendrene, B; 1423, unidentified, B,D; 1425, unidentified, B; 1428,  $\alpha$ -cadinene, B,D; 1433,  $\alpha$ -humulene, A,B,C,D; 1436, sesquiterpene, C; 1445, *n*-dodecanol, B; 1457, sesquiterpene, B; (1457,  $\gamma$ -muurolene, A,B,C,D; 1459, germacrene D, A,B,C,D; 1462,  $\alpha$ -cucumene, B,D; 1463, unidentified, A,B,C,D; 1465,  $\beta$ -cubebene, B,D; 1471,  $\alpha$ -elemene, B,C; (1478,  $\alpha$ -selenene, D); 1482,  $\alpha$ -muurolene, B,D; (1496,  $\alpha$ -farnesene, B,C,D); 1499, calamenene, B,D; 1499, unidentified, B,D; 1515, oxygenated sesquiterpene, B,D; 1521,  $\gamma$ -elemene, A,B,C,D; 1537, nerolidol, A,B; (1547, diethyl-phthalate, D); 1549, cedrol, C; 1570, sesquiterpene alcohol, B,C; 1590, sesquiterpene alcohol, B; 1604, taucadinol, B,D; 1613, torreyol, B,D; 1618,  $\beta$ -eudesmol, C; 1620,  $\alpha$ -cadinol, B,C; 1626,  $\alpha$ -eudesmol, C. From the retention times and mass spectral fragmentation pattern the identification of allyl acetate as one constituent of the volatile leaf oil is definite. However, because there is no previous report that allyl esters occur naturally, the possibility of an uncontrolled source of contamination cannot be eliminated. Diethyl-phthalate also has not been unequivocally shown to be a naturally occurring constituent, but it has recently been reported that diethylphthalate was found in diethyl ether extracts of wheat leaves (14), and an increase

<sup>1</sup>Compound designations in parentheses denote tentative identification.

TABLE 1. Composition of the Oil Fraction Steam Distilled From the Leaves of *Salvia brandegei*, *Salvia columbariae*, *Salvia mellifera*, and *Salvia munzii*

Compound	RRT	Total oil (%)			
		A <i>Salvia brandegei</i>	B <i>Salvia columbariae</i>	C <i>Salvia mellifera</i>	D <i>Salvia munzii</i>
$\alpha$ -pinene . . . . .	922	5.0	4.3	2.7	7.1
camphene . . . . .	931	3.0	0.6	2.8	3.0
$\beta$ -pinene . . . . .	980	4.8	6.8	3.3	4.1
myrcene . . . . .	992	1.2	4.5	0.8	1.4
$\alpha$ -phellandrene . . . . .	1001	(t)	1.5	(t)	(t)
3-carene . . . . .	1009	(t)	2.9	(t)	0.7
<i>p</i> -cymene . . . . .	1012	0.4	1.5	0.5	0.5
1,8-cineole . . . . .	1020	19.2 <sup>a</sup>	24.3 <sup>a</sup>	14.5 <sup>a</sup>	17.5 <sup>a</sup>
$\beta$ -phellandrene . . . . .	1021	0.0 <sup>a</sup>	14.2 <sup>a</sup>	1.5 <sup>a</sup>	8.2 <sup>a</sup>
limonene . . . . .	1024	17.1	5.8	1.6	14.1
<i>cis</i> -ocimene . . . . .	1032	2.5	(t)	0.7	(t)
<i>trans</i> -ocimene . . . . .	1042	(t)	1.3	(t)	(t)
$\gamma$ -terpinene . . . . .	1050	0.9	2.5	0.9	0.6
terpinolene . . . . .	1084	0.6	0.9	0.5	0.5
linalool . . . . .	1085	0.5	(t)	(t)	(t)
camphor . . . . .	1113	36.1	8.6	62.4	29.2
borneol . . . . .	1142	0.5	(t)	1.0	1.0
4-terpineol . . . . .	1157	0.5	(t)	0.6	(t)
$\alpha$ -terpineol . . . . .	1168	1.7	(t)	(t)	(t)
bornyl acetate . . . . .	1261	(t)	(t)	(t)	1.9
$\beta$ -caryophyllene . . . . .	1400	0.4	2.3	0.6	2.7
unknown sesquiterpene . . . . .	1444	(t)	0.8	(t)	(t)
unknown sesquiterpene . . . . .	1479	(t)	0.5	(t)	(t)
$\gamma$ -cadinene . . . . .	1495		0.7	(t)	(t)
$\Delta$ -cadinene . . . . .	1500	(t)	0.8	(t)	(t)
farnesol . . . . .	1662		1.3		

<sup>a</sup>Value estimated from ITD (mass spectral) data.

TABLE 2. Localities of Representative Populations of *Salvia**Salvia brandegei*

1. Punta Cabras, Baja California Norte, Mexico

*Salvia columbariae*

1. Caravina, Baja California Norte, Mexico
2. El Rosario, Baja California Norte, Mexico
3. 5 km west of Lake Elsinore, Riverside County, California
4. Reche Canyon, Riverside County, California
5. Elizabeth Lake, Los Angeles County, California

*Salvia mellifera*

1. Santa Catalina Island, Los Angeles County, California
2. Salinas, Monterey County, California
3. Nacimiento-Fergusson Road, Monterey County, California
4. University of California Motte-Rimrock Reserve, Riverside County, California
5. Sage, Riverside County, California
6. Jack Rabbit Trail, Riverside County, California
7. Cuesta Ridge, San Luis Obispo County, California

*Salvia munzii*

1. San Telmo—Mehling Ranch Road, western foothills of the Sierra San Pedro Martir, Baja California Norte, Mexico
2. Otay Reservoir, San Diego County, California

of diethyl phthalate was observed to occur during fermentation of honeysuckle berry wine, *Lonicera edulis* (15). The widespread use of phthalate esters as an industrial chemical and its general dissemination into the environment makes it difficult to determine whether phthalate esters are really naturally occurring.

#### EXPERIMENTAL

Five to ten plants from different collection sites per population (Table 2) and one to several populations per species were grown from seeds or cuttings at the University of California at Riverside. Harvests were made between 8:00 and 10:00 AM to minimize diurnal effects. Bulk averaged equal weights of fresh leaves from each plant per population were steam distilled for 1 h. Oils were kept at  $-20^{\circ}$  until analyzed with a Varian 6000 GC using a 0.25 mm id  $\times$  30 m DB-1 fused silica capillary column employing both flame ionization detection (FID) and Finnigan ion trap detection (ITD) systems. Mass spectra of all components were obtained by the Finnigan ion trap detector system employing multiple ion detection with 10 tuning segments, the  $m/z$  ranges including: (a) 43-50; (b) 51-64; (c) 65-90; (d) 91-100; (e) 101-110; (f) 111-147; (g) 148-174; (h) 175-200; (i) 201-240; (j) 241-280.

Identifications were made by comparisons by both retention times and mass spectra with those of standards and of known terpenes in juniper oils (5-9). Relative retention times, RRT, are listed following the procedure of Jennings and Shibamoto (10) where the last two digits indicate the percent fraction of the actual elution between the elution times of two consecutive normal alkanes and where the carbon number of the lower alkane is indicated by the digits preceding the percent fraction. Additional identifications were made based upon a number of reference sources which contained RRT and mass spectral data (11-13). Compounds for which no standards were available, but which matched published mass spectral data and eluted with correct retention times relative to known compounds, were given tentative identifications.

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