

THE VOLATILE LEAF OILS OF THE JUNIPERS OF GUATEMALA AND CHIAPAS, MEXICO:  
*JUNIPERUS COMITANA*, *JUNIPERUS GAMBOANA*, AND *JUNIPERUS STANDLEYI*

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Three juniper species are native to Guatemala and Chiapas, Mexico: *Juniperus comitana* Mart., *Juniperus gamboana* Mart., and *Juniperus standleyi* Steyermark (1). Each of these species is endemic to the high mountains along the border of Guatemala and Chiapas, Mexico (2). *J. comitana* occurs on limestone hills, in pine-oak and *Ficus-Acacia* forests in the mountains of Chiapas, and on rocky hills in Guatemala at 1300-2300 m elevation (1,2). *J. gamboana* grows on limestone at 1670-2200 m in Chiapas and Departamento Huehuetenago, Guatemala (1,2). *J. standleyi* is found above timberline on Volcano Tacana in Chiapas and at elevations of 3000 m or higher in Departamento Huehuetenago, Guatemala (1,2). The ranges of these taxa are very restricted, and these species apparently have been isolated from the other junipers of the western hemisphere since Tertiary times (3). Although a recent study found prominent *Juniperus* pollen deposits in lake sediments dated at 8,815 and 10,750 b.p. (4), the geographically closest extant juniper population to the Pleistocene deposits is *J. comitana*, 200 km south and west at Baja Verapaz and Chiapas (4). Leyden (4) postulated that *J. comitana* descended 500 to 1000 m during arid portions of the Pleistocene in Guatemala. In any case, the ranges of these three taxa of *Juniperus* have not been extensive in recent geological time.

Although we have previously reported on the terpenoid similarities via numerical taxonomic procedures (3), this paper presents the first detailed identification of the steam-volatile leaf oil components of these junipers.

## MATERIALS AND METHODS

**PLANT MATERIALS.**—Fresh foliage was kept frozen until steam distilled and the following samples were collected: *J. comitana*, on Rt. 17, 19 km east of Rt. 190, Municipio de la Trinitaria, Chiapas, Mexico (Zanoni voucher #2654); *J. gamboana*, 14 km north of Comitán, Chiapas, Mexico on Rt. 190 (Zanoni voucher #2664); and *J. standleyi*, 26 km north of the city of Huehuetenago, Guatemala on the RN 9 N road to San Juan Ixcóy (Zanoni voucher #2644). Voucher specimens are deposited at the University of Texas at Austin. The volatile leaf terpenoids were isolated by the steam distillation of approximately 200 g of foliage for 2 h (5). The oils were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and kept tightly sealed in glass vials with foil-lined caps at -20° until analyzed.

Mass spectra were recorded with a Finnigan 4000 quadrupole gas chromatograph/mass spectrograph system using a deactivated SP2100 glass capillary column, 0.25 mm i.d. × 30 m [see Adams *et al.* (6) for conditions]. Quantification was made by FID using a deactivated SP2100 glass capillary column (as above) on a Varian 1860 with N<sub>2</sub> as a carrier gas at an average linear velocity of 12 cm/sec, temperature programmed as: initial temperature, 70°; then 1.5°/min for 18 min; 2.5°/min for 24 min; 6°/min for 6 min; 4°/min for 6 min; and isothermal at 217° for 6 min. Butyl acetate and hexadecyl acetate were added as internal standards. These compounds were chosen as standards because butyl acetate elutes before the more volatile terpenes and hexadecyl acetate elutes after most terpenes found in these oils.

Identifications were made by comparisons of the mass spectrum of each component in the oils with those of the known terpenes and searches of spectra from the Finnigan library based on National Bureau of Standards (NBS) data. Relative retention times (RRT hexadecyl acetate = 1.00) were also compared to the RRT of known terpenoids run under the same conditions.

## RESULTS

The oils were light to medium yellow with yields from 1-3% dry weight. The composition of these three taxa are shown in Table 1. The volatile leaf oil composition of *J. comitana* is unusual in that only one component (bornyl acetate, 16.2%) is greater than 10% of the oil (Table 1). In contrast, the leaf oil of *J. gamboana* is dominated by  $\alpha$ -pinene (45.1%) and *J. standleyi* (Table 1) is dominated by sabinene (36.0%), 4-terpineol (13.6%), and bornyl acetate (11.0%). *J. comitana* has several compounds that are unique in juniper leaf oils so far analyzed (7-15) such as 2-nonanol, valencene,  $\alpha$ -longipinene, and cedrol (Table 1).

TABLE 1. Composition of the Volatile Leaf Oils of *Juniperus comitana*, *Juniperus gamboana*, and *Juniperus standleyi* (Compounds are listed in order of their elution on OV1)

Compound <sup>a,b</sup>	Percent total oil <sup>c</sup>		
	<i>J. comitana</i>	<i>J. gamboana</i>	<i>J. standleyi</i>
tricyclene . . . . .	—	t	t
α-thujene . . . . .	—	—	1.3
α-pinene . . . . .	7.8	45.1	2.7
camphene . . . . .	(t)	0.7	t
[bicyclo(3,2,1)-oct-2-ene, 3 me-4-methylene] . . . . .	—	2.4	0.7
sabinene . . . . .	(t)	(t)	36.0
β-pinene . . . . .	2.4	5.5	(t)
7-octen-4-ol . . . . .	t	t	—
myrcene . . . . .	4.7	4.5	3.2
4-carene . . . . .	—	—	t
α-phellandrene . . . . .	—	t	t
3-carene . . . . .	t	3.6	t
α-terpinene . . . . .	—	—	2.6
p-cymene . . . . .	t	t	0.5
β-phellandrene . . . . .	2.1	2.4	t
limonene . . . . .	5.6	1.6	4.2
trans-ocimene . . . . .	t	t	t
γ-terpinene . . . . .	t	t	4.3
β-terpineol isomer . . . . .	—	—	2.1
p-cymenene . . . . .	—	t	—
terpinolene . . . . .	t	0.5	1.3
nonanal . . . . .	—	—	t
β-terpineol . . . . .	—	—	1.8
unknown 1, C <sub>10</sub> -OH, RRT=0.324 . . . . .	—	0.8	—
linalool . . . . .	1.6	1.4	t
2-nonanol . . . . .	0.7	—	—
isothujone . . . . .	—	—	t
unknown 2, C <sub>10</sub> -OH, RRT=0.339 . . . . .	2.0	1.1	—
(cis)-dihydrocarveol . . . . .	t	t	0.8
camphor . . . . .	1.2	0.6	0.7
trans-pinocarveol . . . . .	1.5	0.7	(t)
(trans)-dihydrocarveol . . . . .	(t)	—	0.6
camphene hydrate . . . . .	1.7	0.5	—
(isogeraniol) . . . . .	2.8	0.9	—
(cis)-verbenol . . . . .	0.7	0.8	—
iso-pinocamphone . . . . .	t	t	—
borneol . . . . .	—	1.0	1.1
unknown 3, C <sub>10</sub> -OH, RRT=0.387 . . . . .	2.5	0.7	—
4-terpineol . . . . .	0.8	t	13.6
myrtenal . . . . .	t	(t)	—
α-terpineol . . . . .	2.9	1.0	0.5
verbenone . . . . .	1.3	1.0	(t)
myrtenol . . . . .	0.6	t	—
fenchyl acetate . . . . .	1.1	t	—
trans-carveol . . . . .	0.9	t	—
myrtenyl acetate . . . . .	—	1.0	t
cironellol . . . . .	—	t	t
piperitone . . . . .	—	(t)	t
(sabinol) . . . . .	—	0.6	—
bornyl acetate . . . . .	16.2	4.4	11.0

TABLE 1. *Continued*

Compound <sup>a,b</sup>	Percent total oil <sup>c</sup>		
	<i>J. comitana</i>	<i>J. gamboana</i>	<i>J. standleyi</i>
safrole . . . . .	2.8	t	—
carvacrol methyl ether . . . . .	—	—	1.7
thymol . . . . .	—	t	—
methyl eugenol . . . . .	1.0	t	—
caryophyllene . . . . .	1.8	0.7	t
α-cadinene . . . . .	(t)	0.5	—
α-humulene . . . . .	(t)	t	(t)
germacrene, isomer 1 . . . . .	t	1.6	(t)
germacrene, isomer 3 . . . . .	(t)	t	—
germacrene D . . . . .	4.9	0.5	t
valencene . . . . .	0.6	—	—
α-murolene . . . . .	(t)	0.9	(t)
(α-longipinene) . . . . .	0.9	—	—
γ-cadinene . . . . .	(t)	2.2	t
calamanene . . . . .	(t)	0.6	—
Δ-cadinene . . . . .	0.5	3.2	t
unknown 4, C <sub>15</sub> -OH, RRT=0.692 . . . . .	t	1.1	—
elemicin . . . . .	—	t	—
elemol . . . . .	5.3	—	1.1
γ-elemene . . . . .	1.9	(t)	(t)
β-bisabolene . . . . .	t	—	—
unknown 5, C <sub>15</sub> -OH, RRT=0.715 . . . . .	1.2	—	—
unknown 6, C <sub>15</sub> -OH, RRT=0.715 . . . . .	—	1.8	—
cedrol . . . . .	1.2	—	t
[4-(2,6,6-trimethyl-1-cyclo- hexane-1-yl)-(E)-3- butene-2-one]			
(cubenol) . . . . .	(t)	t	t
γ-eudesmol . . . . .	2.2	(t)	t
α-cadinol isomer . . . . .	1.3	4.7	t
torreyol . . . . .	—	1.1	—
β-eudesmol . . . . .	2.7	t	0.7
α-eudesmol . . . . .	3.9	—	t
cadinol isomer . . . . .	—	6.5	—
mannyloxide . . . . .	0.7	t	t

<sup>a</sup>Compound names in parenthesis or brackets are tentatively identified.

<sup>b</sup>Compositional values in parenthesis indicate that a compound runs at that retention time but no spectrum was obtained.

<sup>c</sup>Trace (t) indicates the compound was less than 0.5% of the total oil.

However, cedrol is common in the heartwood oil of junipers (16-18). *J. gamboana* had no very unusual components but an extremely diverse array (66) of compounds. The presence of carvacrol methyl ether in *J. standleyi* is unusual in the denticulate leaf junipers of North America (7-12).

The six compounds occurring in the oils that remain unidentified are: 1, RRT=0.324, mw 152, *m/z* (%) 96(100), 109(65), 43(58), 67(42), 79(30), a terpene alcohol; 2, RRT=0.339, mw 152, *m/z* (%) 108(100), 93(67), 41(46), 67(28), 95(26), a terpene alcohol; 3, RRT=0.387, mw 152, *m/z* (%) 59(100), 94(66), 79(57), 43(33), 91(33), a terpene alcohol; 4, RRT=0.692, mw 222, *m/z* (%) 43(100), 95(58), 41(48), 55(46), 109(34), a sesquiterpene alcohol; 5, RRT=0.715, mw 222, *m/z* (%) 41(100), 43(68), 79(61), 93(55), 69(48), a sesquiterpene alcohol; 6, RRT=0.715, mw 222, *m/z* (%) 43(100), 81(97), 41(76), 79(51), 93(47), possibly an alcohol of β-elemene.

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CONSTITUENTS FROM *CHRYSACTINIA MEXICANA*

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The small genus *Chrysactinia* previously was part of the subtribe Tageteae (Compositae, Tribe Heleniae), but recently has been transferred to the subtribe Pectidinae in the tribe Heliantheae (1). Little is known of the chemistry of the genus *Chrysactinia*; only some diverse compounds are reported from *Chrysactinia mexicana* A. Gray (2), which show no chemotaxonomic relationship to compounds typical of this subtribe.

We, therefore, have reinvestigated this species. The extract of the aerial part gave the thiophene derivatives **1-4**, which are characteristic for the genus *Tagetes* and related genera, and **3Z**, **6Z**, **8E**-dodecatriene-1-ol (**5**) (3). The structures of **1-4** were determined by direct comparison with authentic material.<sup>1</sup> The presence of **5**, which previously has been isolated as a termite trail-following pheromone (3), could be established by mass spectroscopy and by <sup>1</sup>H-nmr spectroscopy. The configurations of the double bonds followed from the couplings, while the positions were deduced by spin decoupling, which gave the whole sequence.

The isolation of **1-4** supports the position of the genus *Chrysactinia* in the subtribe Tageteae (4).

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