

THE VOLATILE LEAF OILS OF TWO RARE JUNIPERS FROM WESTERN MEXICO:
JUNIPERUS DURANGENSIS AND *JUNIPERUS JALISCANA*

ROBERT P. ADAMS

Science Research Center, Hardin-Simmons University, 8555 S. Escalante Dr., Sandy, Utah 84092

THOMAS A. ZANONI

Jardin Botanico Nacional, Dr. Rafael M. Moscoso, Santo Domingo, Dominican Republic

and LAWRENCE HOGGE

*Plant Biotechnology Institute, National Research Council of Canada,
Saskatoon, Saskatchewan, S7N 0W9 Canada*

Juniperus durangensis Mart. is a small tree with scale leaves that resemble a string of beads (1). The taxon is rare and threatened in its natural habitat in the Sierra Madre Occidental mountains of western Mexico, where it is known from only scattered locations at 1600-2900 m (2). *Juniperus jaliscana* Mart. is a tree growing up to 10 m with a very restricted distribution in western Mexico. It is currently found in only two locations: around the village of Cuale, Jalisco (1335-1600 m) and near Pueblo Nuevo, Durango, at 2670 m (1). *J. jaliscana* is extremely rare and should be considered endangered because of the disruption of its habitat by logging and firewood-gathering in the area.

Although we have reported previously 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 collected and kept frozen until steam distilled: *J. durangensis*, from north of km 152 on Rt. 40 at Puerto Buenos Aires, Durango, Mexico, (Zanoni 2741); and *Juniperus jaliscana*, on the hills around Cuale, Jalisco, Mexico, (Zanoni 2540). 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 (4). The oils were dried over anhydrous Na₂SO₄ and kept tightly sealed in glass vials with foil lined caps at -20° until analyzed.

Mass spectra were recorded with a Finnigan 4000 quadrupole gc/ms system using a deactivated SP-2100 glass capillary column, 0.25 mm i.d. × 30 m, under conditions described by Adams *et al.* (5). Quantification was made by FID using a deactivated SP-2100 glass capillary column (as above) on a Varian 1860 with N₂ 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 by 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 with the RRT of known terpenoids run under the same conditions.

RESULTS

Oils were light-to-medium yellow with yields from 1 to 3% dry weight. The composition of these two taxa is shown in Table 1.

J. durangensis is characterized by a large amount of α -pinene (68.4%) and moderate amounts of other monoterpene hydrocarbons such as β -pinene, myrcene, 3-carene, limonene, and terpinolene (Table 1). Oxygenated monoterpenes and sesquiterpenes are noticeably very minor components. In contrast, *J. jaliscana*, although also high in α -pinene (37.0%) and limonene (20.9%) has moderate amounts of linalool, 4-terpineol, bornyl acetate, germacrene, γ -cadiene, Δ -cadiene, and cadinol (Table 1). The components derived from the phenylpropanoid pathway (e.g. methyl eugenol) are very minor, as has been the case in most of the denticulate leaf junipers of the western hemisphere (6-11). In contrast, the integre (smooth leaf) section has been found to contain appreciable amounts of compounds derived from the phenylpropanoid pathway (12-14), except for the closely related species of Hispanola, *Juniperus ekmanii* Florin and *Juniperus gracilior* Pilger, whose leaf oils were dominated by bornyl acetate (13-14).

Neither *J. durangensis* nor *J. jaliscana* had compounds that are unusual in the leaf oils of the junipers of the western hemisphere (6-14). Despite the small, isolated populations of these two taxa, we find no tendency for genetic drift toward an exceptionally unusual volatile oil profile.

TABLE 1. Composition of the Volatile Leaf Oils of *Juniperus durangensis* and *Juniperus jaliscana* (Compounds are listed in order of their elution from an OV1 column.)

Compound ^{a, b}	total oil ^c (%)	
	<i>J. durangensis</i>	<i>J. jaliscana</i>
α-Pinene	68.4	37.0
α-Fenchene	t	—
Camphene	t	0.6
[Bicyclo (3,2,1)-oct-2-ene, 3 Me-4-methylene]	1.0	t
Sabinene	(t)	t
β-Pinene	2.2	3.0
Myrcene	2.6	5.1
3-Carene	10.7	t
p-Cymene	0.5	t
β-Phellandrene	0.5	1.0
Limonene	2.2	20.9
trans-Ocimene	t	t
γ-Terpinene	—	0.6
Terpinolene	1.0	1.2
Linalool	t	3.3
Unknown 1, C ₁₀ -OH, RRT=0.339	0.6	0.9
cis-Dihydrocarveol	—	t
Camphor	t	1.2
trans-Pinocarveol	0.7	t
Camphene hydrate	t	t
trans-Sabinene hydrate	—	t
Unknown 2, C ₁₀ -OH, RRT=0.368	0.5	t
(Isogeraniol)	t	t
Iso-Pinocamphone	(t)	t
Unknown 3, C ₁₀ -OH, RRT=0.387	0.7	0.7
4-Terpineol	t	1.2
3,7,7-Trimethyl-bicyclo-(3.1.1)-2-heptanone	t	(t)
Verbenone	0.7	t
Myrtenol	t	—
Fenchyl acetate	—	t
trans-Carveol	—	t
Thymol methyl ether	t	t
Myrtenyl acetate	(t)	0.7
Borynl acetate	(t)	6.1
Carvacrol methyl ether	t	—
Thymol	—	t
Methyl eugenol	1.0	t
Caryophyllene	t	t
α-Cadinene	t	0.8
α-Humulene	t	(t)
Germacrene, isomer 1	—	2.2
Germacrene D	—	0.9
α-Murolene	(t)	t
γ-Cardinene	t	1.7
Calamanene	t	0.7
Δ-Cadinene	t	1.4
Unknown 4, C ₁₅ -OH, RRT=0.715	—	1.2
[4-(2,6,6-Trimethyl-1-cyclohexane-1-yl)-(E)-3-butene-2-one]	—	t
α-Cadinol isomer	—	5.4
Cadinol isomer	—	3.5
Mannyloxide	—	1.1

^aCompound names in parenthesis or brackets are tentatively identified.

^bCompositional values in parentheses indicate that a compound runs at that retention time but no spectrum was obtained.

^ct indicates the compound was present only in trace amounts, 0.5% of the total oil.

The four compounds occurring in the oils that remain unidentified are: 1. RRT=0.339, MW152, *m/z* (%) 108(100), 93(67), 41(46), 67(28), 95(26), a monoterpene alcohol; 2. RRT=0.368, MW150, *m/z*(%) 91(100), 41(78), 94(45), 109(43), 79(42), a monoterpene alcohol; 3. RRT=0.387, MW152, *m/z*(%) 59(100), 94(66), 79(57), 43(33), 91(33), a monoterpene alcohol; and 4. RRT=0.715, MW222, *m/z*(%) 43(100), 81(97), 41(76), 79(51), 93(47), possibly an alcohol of β -elemene.

ACKNOWLEDGMENTS

We would like to thank NSF for continued support of chemosystematic studies in *Juniperus* (grants GB24320, GB37315X, DEB77-22331 to RPA) and to the staff of the National Research Council of Canada, Plant Biotechnology Institute, Saskatoon, Saskatchewan, Canada.

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Received 4 February 1985

C-GLYCOSYLFLAVONES FROM *MONNIERIA TRIFOLIA*

A. KEITA,

Office malien de Pharmacie, Bamako, Mali

J. GLEYE, E. STANISLAS,*

Faculté des Sciences Pharmaceutiques, Université Toulouse III, France

et I. FOURASTE

Faculté de Pharmacie, Université Montpellier I, France

We have previously reported alkaloids from the leaves of *Monnieria trifolia* L. (Rutaceae, Cuspariae) (1, 2). Recently, other alkaloids have been isolated from the leaves (3) and whole plant (4). In the present work the leaves of *M. trifolia* yielded four di-C-glycosylflavones: neoschaftoside, vicenin-3, schaftoside, and isoschaftoside.

EXPERIMENTAL

PLANT MATERIAL.—The leaf material was collected from plants grown in French Guyana. A voucher specimen has been deposited at the Herbarium of the Faculté des Sciences Pharmaceutiques, Toulouse, France.

EXTRACTION AND ISOLATION OF FLAVONES.—Air-dried leaves of *M. trifolia* were exhaustively extracted with MeOH. The concentrated MeOH extract was chromatographed on an Amberlite XAD₂ column with the following eluants: H₂O and NH₄OH (5%). The basic fraction, after neutralization, was extracted successively with Et₂O, EtOAc, and *n*-BuOH. The *n*-BuOH fraction contained most of the flavonoids.