FLAVOUR AND FRAGRANCE JOURNAL, VOL. 2, 33–36 (1987)

The Volatile Leaf Oils of the Junipers of Cuba: *Juniperus Lucayana* Britton and *Juniperus Saxicola* Britton and Wilson

Robert P. Adams

Box 423, Baylor University, Waco, Texas 76798, USA

Antonio Lopez Almirall

Instituto de Botanica A.C., Cerro 1257, Habana 6, Cuba

Lawrence Hogge

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

The junipers of Cuba are *Juniperus lucayana* and *J. saxicola*, the latter being endemic to Pico Turquino in Cuba. In this first report on the oils of the junipers of Cuba, the leaf oils were first extracted and then analysed by GC–MS. *Juniperus lucayana* from mainland Cuba and the Isle of Pines had oil yields (oven dry weight basis) of 0.58% (2 h) and 2.33% (24 h), and 0.40%(2 h), and 1.58% (24 h), respectively. The oils are dominated by α-pinene (25–27%), limonene (23–27%), sabinene (11–12%) with small amounts of sesquiterpenes. The volatile leaf oil of *J. saxicola* was obtained in yields (oven dry weight basis) of 0.30% (2 h) and 0.72% (24 h). Its oil is dominated by sabinene (25%) and α-pinene (24%), and is more similar to *J. lucayana* than other species of the Caribbean. The oil compositions of other junipers of the Caribbean are included to aid in making comparisons.

KEY WORDS Essential oils *Juniperus lucayana* *Juniperus saxicola* Cupressaceae Terpenes

INTRODUCTION

The junipers of Cuba consist of only two species: *Juniperus lucayana* Britton and *J. saxicola* Britton and Wilson according to Florin.[1] Carabia[2] treated *J. lucayana* as a synonym of *J. barbadensis* L. and this question is currently being reinvestigated.[3] For the present, we will follow Florin. *Juniperus lucayana* (*sensu* Florin) occurs naturally on Great Abaco, Andros, and Grand Bahama Islands of the Bahamas and possibly on New Providence and other islands. It also occurs on Jamaica (Blue Mts) but appears to now be extinct in Hispaniola.[4] In Cuba, *J. lucayana* was reported by Carabia[2] to be in Pinar del Rio, Santa Clara, Oriente and the Isla de Pinos (Isle of Pines) in swampy areas. In Oriente it was said to be quite abundant on the Sierra de Nipe. The range has apparently markedly decreased in Cuba owing to draining of marsh land for cultivation. *Juniperus saxicola* is endemic to Cuba and is known only from its type locality, Pico Turquino in the Sierra Maestra at 1000 to 2000 m elevation.[2] *Juniperus saxicola* is very unusual in that it produces only the awn-shaped (juvenile) leaves which are normally found on young plants or at the tips of fast growing branchlets in the junipers of the section *Sabina*. This species, by neoteny, is apparently stabilized in the juvenile morphological state. Previous examination of the volatile leaf oils of mature and juvenile leaves of *J. horizontalis*[5] revealed essentially no significant differences in the composition and in the case of *J. scopulorum*[6] showed several minor differences comparable to the effects of seasonal variation but smaller than specific differences.

This study presents the composition of the volatile leaf oils from *J. lucayana* from the mainland Cuba and from the Isle of Pines and the oil of *J. saxicola* collected from the type locality, Pico Turquino. These are compared to the oils of other Caribbean junipers.

0882–5734/87/010033–04$05.00

Received 24 March 1987

Table 1. Composition of the volatile leaf oils of the junipers from Cuba along with other Caribbean junipers previously reported. Compounds are listed in order of their elution from a DB1 column

Compound	Percentage total oil								
	[a]SX	LC	LP	LJ	LB	VS	BM	EK	GR
Percentage yield (2 h)	0.3	0.6	0.4	0.6	0.2	0.4	0.3	1.4	0.8
Unknown 1, RRT = 0.143	—	(T)	(T)	—	T	—	—	(T)	0.8
Unknown 2, RRT = 0.151	—	(T)	(T)	—	T	—	—	(T)	0.8
Tricyclene/α-Thujene	1.1	0.6	T	0.6	0.5	T	T	1.9	1.4
α-Pinene	24.4	25.6	27.4	49.1	33.0	2.4	22.3	1.3	1.8
Camphene	T	T	T	T	T	T	0.7	1.9	1.2
Sabinene	25.2	12.1	11.1	9.7	8.3	T	2.8	5.0	10.1
β-Pinene	T	0.5	1.3	1.1	1.2	T	0.6	T	T
Oct-1-en-3-ol	—	—	—	T	T	0.9	1.0	T	T
Myrcene	2.7	3.2	2.3	3.2	4.0	0.9	2.9	2.5	1.9
Car-2-ene	—	—	—	T	T	T	—	T	—
α-Phellandrene	T	T	T	—	—	—	T	—	T
Car-3-ene	T	—	T	—	—	T	T	—	—
α-Terpinene	2.4	1.1	1.0	T	T	T	T	0.9	1.7
p-Cymene	0.8	T	0.5	T	T	T	0.5	0.5	1.4
β-Phellandrene	T	—	—	—	—	—	—	—	—
Limonene	2.6	23.2	27.4	25.9	18.0	33.3	35.3	9.6	7.3
trans-Ocimene	T	—	—	T	—	—	T	—	—
γ-Terpinene	3.7	1.8	1.7	0.8	0.7	T	0.7	1.7	3.5
(*p*-Menth-1(7),3-diene)	0.7	—	—	T	—	—	T	—	—
(*cis*-*p*-Menth-2-en-ol	—	T	T	—	T	—	—	0.9	1.1
Terpinolene	1.2	0.8	0.8	1.0	0.8	(T)	0.8	0.6	0.9
(*trans*-*p*-Menth-2-en-ol	T	T	T	—	—	—	—	—	T
Terpinen-4-yl acetate	T	—	—	T	—	—	—	—	—
Linalol	—	0.7	T	—	T	1.5	1.1	(0.6)	2.6
Unknown 3, RRT = 0.337	—	—	—	—	—	—	(T)	1.6	2.0
(3-Cyclopentene-1-acetaldehyde, 2,2,3-tri-methyl)	—	—	—	T	T	—	T	—	—
cis-Sabinene hydrate	T	—	—	T	T	—	T	—	—
(*cis*-dihydrocarveol)	—	T	T	—	—	—	—	0.5	0.8
Camphor	2.8	0.9	T	T	T	T	6.5	5.8	1.1
trans-Pinocarveol	—	—	—	—	—	—	1.1	—	—
(*trans*-dihydrocarveol)	—	T	T	T	(T)	—	—	(T)	0.7
trans-Sabinene hydrate	T	—	—	—	—	—	—	—	—
Camphene hydrate	—	—	—	—	(T)	T	1.4	2.2	1.4
Borneol	—	T	T	T	T	—	2.1	5.1	2.0
Terpinen-4-ol	5.9	3.7	2.9	1.6	2.5	T	1.4	6.3	11.6
Myrtenal	—	—	—	—	(T)	T	0.7	—	—
α-Terpineol	T	T	T	T	T	—	T	0.8	0.9
Estragol	—	T	T	—	—	0.5	—	—	—
(*p*-Cymen-8-ol)	—	—	—	T	T	T	T	—	—
cis-Piperitol	T	—	—	—	—	—	—	T	T
Unknown 4, RRT = 0.426	—	—	—	—	—	—	—	(T)	1.2
Carvone	—	—	—	T	(T)	T	1.0	(T)	T
Citronellol	T	T	T	T	0.9	T	T	(0.6)	0.6
Piperitone	—	—	—	—	0.6	T	—	—	T
Isosafrole	0.6	—	—	—	(T)	3.6	(T)	—	—
Bornyl acetate	T	1.3	2.5	0.6	4.1	T	4.2	43.9	35.7
Safrole	—	—	0.7	T	(T)	13.7	—	—	(T)
Sabinyl acetate	—	—	T	—	T	—	0.8	(T)	(T)
Methyl eugenol	—	—	T	T	(T)	8.2	(T)	—	T
Caryophyllene	T	T	T	T	T	T	T	T	T
Thujopsene	T	T	—	—	(T)	(T)	2.1	(T)	T
α-Cadinene	—	0.6	0.6	—	T	—	—	T	T
Germacrene isomer 2	—	0.7	0.6	—	T	T	—	T	T
Germacrene D	2.5	T	T	0.6	T	(T)	T	—	—
β-Cubebene	—	1.6	1.3	—	0.8	—	—	T	T
Unknown 5, RRT = 0.658	—	0.6	T	—	0.9	—	—	—	—

Compound	Percentage total oil								
	[a]SX	LC	LP	LJ	LB	VS	BM	EK	GR
αMuurolene	T	T	T	T	—	T	T	T	T
γ-Cadinene	T	1.6	0.9	—	2.8	T	—	T	—
δ-Cadinene	T	1.9	1.7	T	0.7	0.7	T	T	T
(α-Muurolyl oxide)	—	T	—	—	T	—	—	—	—
Elemicin	—	T	2.1	—	—	1.0	—	T	T
Elemol	1.8	T	—	T	T	11.1	T	—	—
Nerolidol	T	T	T	—	—	—	—	—	—
Cadinol isomer 1	—	—	—	T	—	—	—	—	—
Unknown 6, RRT = 0.686	—	0.7	T	—	1.9	0.9	—	—	—
Cadinol isomer 2	—	T	T	T	0.9	(0.8)	—	(T)	(T)
Cedrol	—	—	—	—	—	—	T	T	T
unknown 7, RRT = 0.732	T	2.2	1.3	T	2.2	0.7	T	—	—
(Cubenol)	—	1.9	1.2	—	1.2	(0.7)	T	T	T
γ-Eudesmol	0.8	—	—	—	—	3.4	—	—	—
T-Cadinol	—	—	—	T	—	2.0	—	T	T
T-Muurolol	—	1.1	0.7	—	2.1	—	T	T	—
Cadinol isomer 3	0.6	—	—	—	—	—	—	—	—
Torreyol	—	T	0.8	—	—	—	—	—	—
β-Eudesmol	1.2	—	—	—	—	2.8	—	—	—
Cadinol isomer 4	—	—	—	0.5	—	—	—	—	—
Unknown 8, RRT = 0.769	—	—	—	—	2.3	—	T	(T)	T
α-Cadinol	T	1.0	0.9	—	—	—	—	—	—
α-Eudesmol	1.6	—	—	—	—	3.4	—	—	—
Unknown 9, RRT = 0.782	1.3	—	—	—	—	T	—	—	—
Unknown 10, RRT = 0.791	1.6	0.8	0.6	T	0.9	T	T	T	T
Unknown 11, RRT = 0.795	—	0.5	—	—	—	T	—	—	—
Acetate II	T	—	—	—	—	1.8	—	—	—
Abietatriene	T	T	—	—	T	T	T	—	T
Manool	0.9	—	—	—	T	T	—	—	—
(Kaur-16-ene)	—	0.7	T	—	T	—	0.7	—	T

[a]SX = *J. saxicola*, Cuba; LC = *J. lucayana*, mainland Cuba; LP = *J. lucayana*, Isle de Pines, Cuba; LJ = *J. lucayana*, Jamaica; LB = *J. lucayana*, Bahama Islands; VS = *J. virginiana* var. *silicicola*, Florida, USA; BM = *J. bermudiana*, Bermuda; EK = *J. ekmanii*, Haiti; and GR = *J. gracilior*, Dominican Republic.

EXPERIMENTAL

Plant materials

Fresh foliage was collected and kept cool until steam distilled: *J. lucayana*, cultivated in Habana Botanical Garden, Habana, Cuba, grown from seeds collected from mainland Cuba by J. T. Roig (*Adams* 5279, 5280); *J. lucayana*, cultivated in the National Botanical Garden, Habana, Cuba, originally from Isle of Pines (*Adams* 5281, 5282); and *J. saxicola*, 1550 m, Pico Turquino, Sierra Maestra, Oriente, Cuba (*Adams* 5284, 5285). Voucher specimens are on deposit at the BAYLU herbarium, Baylor University. For information on plant materals, voucher numbers, and oil analyses for *J. bermudiana* (BM), *J. ekmanii* (EK), *J. gracilior* (GR), *J. lucayana* from the Bahamas (LB) and Jamaica (LJ), and *J. virginiana* var. *siliciocola* (VS) see Adams[4] and Adams and Hogge.[7]

The volatile leaf oils were isolated by steam distillation of approximately 200 g of foliage for 2 h.[8] The oils were concentrated under nitrogen, tightly sealed in glass vials with foil-lined caps and stored at −20°C until analysed.

Mass spectra were recorded with a Finnigan 4000 quadrapole GC–MS system using a J & W DB1, 0.25 mm × 30 m, 0.25 micrometre coating thickness, fused quartz capillary column under conditions previously described.[9] Quantification was made by FID using a DB1 column (as above) on a Varian 6500 with He as the carrier gas with an average linear velocity of 30 cm/s, split 1:30, temperature programmed as: initial temperature, 60°C; then 2°C/min to 96°C; then 3°C/min to 156°C; then 6°C/min to 240°C. Butyl and hexadecyl acetates were added as internal standards.[9]

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 the 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 AND DISCUSSION

Oil yields for 2 h (24 h) distillations were: *J lucayana*, mainland Cuba, 0.58% dw (2.33%); *J. lucayana*, Isle of Pines, 0.40% dw (1.58%) and *J. saxicola*, 0.30% dw (0.72%). The composition of the volatile oils of these taxa are shown in Table 1.

The oil of *Juniperus saxicola* (SX in Table 1) is characterized by large amounts of α-pinene and sabinene, and moderate amounts of α-thujene, myrcene, α-terpinene, limonene, γ-terpinene, terpinolene, camphor, terpinen-4-ol, germacrene D, elemol, and α- and β-eudesmols. *Juniperus lucayana* from both mainland Cuba and the Isle of Pines, contained large amounts of α-pinene and limonene, with considerable amounts of sabinene as well as moderate amounts of myrcene, α-terpinene, γ-terpinene, terpinen-4-ol, bornyl acetate, β-cubebene, and various cadinenes. Comparisons with the oils of *J. lucayana* from Jamaica (LJ) and Bahama Islands (LB) from previous studies,[4,7] show the Cuban plants to be quite similar, although both the Jamaican and Bahamian plants have somewhat larger amounts of α-pinene (Table 1). The taxon from southern Florida (*J. virginiana var. silicicola*, VS) is quite different in its volatile leaf oils (note especially isosafrole, safrole, and methyl eugenol from the phenyl propanoid pathway). The Cuban junipers share several oil characteristics with the Bermuda juniper (BM) such as the dominance of α-pinene, and limonene but differ in many compounds (Table 1). The two Junipers from Hispaniola, *J. ekmanii* and *J. gracilior*, are very closely related[4,7] and their oils differ markedly from any of the junipers of the Caribbean with large amounts of bornyl acetate and only moderate amounts of the common monoterpenes so characteristic of the other Caribbean junipers (Table 1).

It would seem probable that *J. saxicola* evolved from *J. lucayana* in Cuba by seed dispersal into the Pico turquino region and subsequent mutation for the fixation of the juvenile leafed form throughout the adult life stage. This hypothesis is further suported by the close similarity of the volatile leaf oils of *J. lucayana* and *J. saxicola*.

Unknowns 1–4, 6, 8, and 10 have been discussed previously.[7] The other unidentified components from Table 1: 5. RRT = 0.658, MW222, *m/z*(%) 161(100), 119(65), 105(62), 43(57), 91(42), 81(40), 55(34), 207(20), a sesquiterpene alcohol; 7. RRT = 0.732, MW220?, *m/z*(%) 43(100), 177(60), 91(28), 107(28), 93(24), 79(24), 95(21), 121(20), 135(19), a sesquiterpene alcohol?; 9. RRT = 0.782, MW222?, *m/z*(%) 59(100), 93(71), 107(56), 43(51), 81(50), 67(47), 161(44), a sesquiterpene alcohol; 11. RRT = 0.795, MW222, *m/z* (%), 84(100), 43(85), 81(73), 55(70), 69(60), 59(48), 82(38), 93(33), a sesquiterpene alcohol. 'Acetate II' has been previously discussed by von Rudloff.[10]

Acknowledgements—We would like to thank the staff from the Primer Simposio Cubano de Botanica, July 2–5, 1985, Habana, and the Academia de Ciencias de Cuba for arranging the field work in Cuba. Special thanks to Mark Donsky for assistance in collecting *J. saxicola*. A portion of this research (work in Bermuda, Bahama, Hispaniola, and Jamaica) was supported by funds from NSF grant DEB79-21757 to RPA.

REFERENCES

1. R. Florin, *Ark. Bot.*, **25A**(5), 1 (1933).
2. J. P. Carabia, *The Caribbean Forester*, **2**, 83 (1941).
3. R. P. Adams, C. E. Jarvis, V. Slane and T. A. Zanoni, *Taxon*, **36**, 441 (1987).
4. R. P. Adams, *Moscosa*, **2**, 77 (1983).
5. R. P. Adams, M. M. Palma and W. S. Moore, *Phytochem.*, **20**, 2501 (1981).
6. R. P. Adams and A. Hagerman, *Biochem. System and Ecology*, **4**, 75 (1976).
7. R. P. Adams and L. Hogge, *Biochem. System and Ecology*, **11**, 85 (1983).
8. R. P. Adams, *Phytochem.*, **9**, 397 (1970).
9. R. P. Adams, M. Granat, E. von Rudloff and L. Hogge, *J. Chromat. Sci.*, **17**, 75 (1979).
10. E. Von Rudloff, *Phytochem.*, **14**, 1319 (1975).