J. Essent. Oil Res., **17**, 103-106 (January/February 2005)

Volatile Constituents of Leaf Oils from the Genus *Baccharis*. Part I: *B. racemosa* (Ruiz et Pav.) DC and *B. linearis* (Ruiz et Pav.) Pers. Species from Argentina**

Rubén A. Malizia, Daniel A. Cardell and José S. Molli
DIPNAYS, Facultad de Ingeniería Química, CONICET-U.N.L, Santiago del Estero 2850, 2do piso, 3000 Santa Fe, Argentina

Silvia González and Pedro E. Guerra
Cátedra de Botánica Forestal, Facultad de Ingeniería, U.N. Patagonia, Cátedra Química Orgánica, Facultad de Ciencias Naturales, U.N. Patagonia, Sarmiento 849, 9200 Esquel, Chubut, Argentina

Ricardo J. Grau*
Instituto de Desarrollo Tecnológico para la Industria Química, CONICET-U.N.L., Güemes 3450, 3000 Santa Fe, Argentina

Abstract

Volatile compounds from *Baccharis racemosa* (Ruiz et Pav.) DC and two samples of *B. linearis* (Ruiz et Pav.) Pers. leaves collected in the Argentinean Patagonia were isolated by steam distillation. Yields on the oils were 2.50% for *B. racemosa*; 0.92% for *B. linearis* (sample A) and 1.91% for *B. linearis* (sample B). The leaf oils were analyzed by GC and GC/MS. The main constituents of each oil were: (i) *B. racemosa* oil: sabinene (13.6%), β-pinene (2.8%), myrcene (2.0%), limonene (13.3%), δ-cadinene (5.3%), (E)-nerolidol (5.0%), viridiflorol (2.6%), α-muurolol (9.7%) and α-cadinol (3.1%); (ii) B. linearis (sample A) oil: α-pinene (6.5%), β-pinene (14.9%), myrcene (2.2%), limonene (27.6%), bicyclogermacrene (2.7%), δ-cadinene (3.9%), caryophyllene oxide (3.1%), cubenol (4.7%) and α-cadinol (4.7%); and (iii) *B. linearis* (sample B) oil: α-pinene (2.5%), β-pinene (6.5%), limonene (27.7%), β-caryophyllene (2.0%), germacrene D (4.7%), bicyclogermacrene (5.4%), δ-cadinene (6.7%), cubenol (6.0%) and α-cadinol (3.0%).

Key Word Index

Baccharis racemosa, *Baccharis linearis*, Asteraceae, essential oil composition, sabinene, β-pinene, limonene, α-muurolol.

Introduction

The genus *Baccharis* L. belongs to Asteraceae family, Tubuliflroideae subfamily, Astereae tribe, comprising more than 400 species of useful aromatic and medicinal plants, widely distributed in central and South America. In Argentina, about 100 species are known and are widely distributed. *Baccharis racemosa* and *B. linearis* (Ruiz et Pav.) Pers. [syn. *B. rosmarinifolia* Hook. et Arn.] (n.v. huencu, romerillo) (Spanish) are distributed in the woods of central and southern Chile, and on the western side of Argentinean Patagonia. They grow in mountainous zones, in sandy soils with gravel, neutral pH and good drainage, mainly along the roads (1-6).

Apparently, there are no previous investigations on the composition of *B. racemosa*. Some results have been reported focusing on the secondary metabolites of *B. linearis* including alkaloids, waxes and diterpenes (7-11). The hybridization of *B. linearis* with *B. macraei* yielded *B. intermedia*, the chemical composition of which has been reported (12). The oleanolic acid content in *B. linearis* and its effects on *Heliothis zea* larvae has also been reported (13). However, few studies on the composition of the volatile oils from these species have been published. In this regard, only one study described the composition of the leaf oil of *B. linearis* by TLC (14). Moreover, there seems to be no previous study on the composition of Argentinean *B. linearis* leaf oil. The present study reports on the oil yields and the compositions of the leaf oils from *B. racemosa* and *B. linearis* growing in Argentinean Patagonia.

**Presented in part at the X Simposio Latinoamericano y VII Simposio Argentino de Farmacobotanica, Comodoro Rivadavia, Argentina, April 8-11, 2001.

*Address for correspondence

Received: March 2002
Revised: September 2002
Accepted: October 2002

1041-2905/05/0001-0103$6.00/0—© 2005 Allured Publishing Corp.

Experimental

Sampling: Specimens were collected in spring from the following places: *B. racemosa*: Presa Futaleufú, Futaleufú Department, Chubut Province, Argentina. *Baccharis linearis* (sample A): Ruta 259, aproximately 3 km from Esquel city, Futaleufú Department, Chubut Province, Argentina. *Baccharis linearis* (sample B): Route 258 - La Burrada (at 15 km of Leleque cross). Voucher specimens have been deposited at the Herbarium of the Department of Forestal Botanics, Faculty of Engineering, National University of Patagonia, Chubut Province, Argentina.

Essential oil: The oil was obtained by hydrodistillation for 3 h using a Clevenger-type apparatus. The samples were subjected to five replications giving an average yield (mL of oil per 100 g of leaves) of 2.50% (standard deviation 0.03%) for *B. racemosa*; 0.92% (standard deviation 0.04%) for *B. linearis* (A); and 1.91% (standard deviation 0.02%) for the second sample of *B. linearis* (B).

Components identification: The constituents of the leaf oils were identified by gas chromatography, using retention indices and chromatographic standards. The retention indices of each file of data were calculated with respect to a set of hydrocarbons of C_7 to C_{23}. The identity of each constituent was checked with the retention time of a pure standard compound on two columns of different polarity. Peak area percentages were calculated from FID area percentages without using either correction factors or an internal standard. The mass spectra were compared to spectra already reported in the literature (15,16) and to those obtained with authentic samples.

Analytical GC: The GC analysis of the oils was performed on a Hewlett Packard 5840A gas chromatograph. Column: DB-5 (30 m x 0.25 mm, film thickness: 0.25 μm). Detector: FID (flame ionization detector). Carrier gas: nitrogen. Split relation: 1:100. Temperature program: initial temperature: 60°C (0 min); incremental increase 4°C/min; final temperature: 300°C (15 min); injector temperature: 250°C; detector temperature: 350°C; injection volume: 0.2 μL.

GC/MS: The GC/MS analysis was performed with a Shimadzu QP-5000 GC/MS equipped with an electronic impact source at 260°C, operating with an emission current of 0.7 mA and 70 eV electron energy. The chromatograph was equipped with columns identical to those used for the GC analysis. A temperature program from 50°-240°C at 6°C/min was used. Carrier gas: helium.

Results and Discussion

Baccharis racemosa yielded 2.50% of a pale yellow liquid (specific gravity 0.884; refractive index 1.4323 at 20°C) with a citrus-like aroma. *Baccharis linearis* (sample A) yielded 0.92% of a pale yellow liquid (specific gravity 0.875; refractive index 1.4445 at 20°C) with a spicy odor. *Baccharis linearis* (sample B) yields 1.91% of a pale yellow liquid (specific gravity 0.878; refractive index 1.4567 at 20°C) also with a spicy odor.

Table I summarizes the qualitative and quantitative analyses of these three leaf oils.

For *B. racemosa*, the main constituents were α-pinene (1.5%), sabinene (13.6%), β-pinene (2.8%), myrcene (2.0%), limonene (13.3%), δ-cadinene (5.3%), (E)-nerolidol (5.0%), viridiflorol (2.6 %), α-muurolol (9.7%) and α-cadinol (3.1%).

For *B. linearis* (sample A), the main constituents were α-thujene (1.8%), α-pinene (6.5%), β-pinene (14.9%), myrcene (2.2%), δ-3-carene (1.6%), limonene (27.6%), terpinen-4-ol (1.6%), β-caryophyllene (1.7%), germacrene D (1.6%), bicyclogermacrene (2.7%), δ-cadinene (3.9%), caryophyllene oxide (3.1%), 1-epi-cubenol (1.6%), cubenol (4.7%), α-muurolol (1.6%) and α-cadinol (4.7%).

For *B. linearis* (sample B), the main constituents were α-pinene (2.5%), β-pinene (6.5%), δ-3-carene (1.3%), limonene (27.7%), linalool (1.5%), β-caryophyllene (2.0%), germacrene D (4.7%), bicyclogermacrene (5.4%), δ-cadinene (1.5%), δ-cadinene (6.7%), ledol (1.6%), 1-epi-cubenol (1.9%), cubenol (6.0%) and α-cadinol (3.0%).

Table II shows the mass spectrum data of some unknown components of *B. racemosa* and *B. linearis* oils.

Table III shows the variation in group contents of the leaf oils from the three species under study. *Baccharis racemosa* oil was richer in monoterpene hydrocarbons (about 36.0%) and oxygenated sesquiterpenes (21.4%). Significant amounts of monoterpene hydrocarbons and sesquiterpene hydrocarbons were found in the *B. linearis* oil. Sample A of *B. linearis* was richer in monoterpene hydrocarbons (57.2% against 41.1%) and lower in sesquiterpene hydrocarbons than sample B (13.7% against 28.2%). Neither diterpene hydrocarbons nor oxygenated diterpenes were found in either *B. racemosa* or *B. linearis* oils.

Acknowledgments

We are grateful to Myriam Calvo for her help in recording GC/MS spectra.

References

1. M. Dimitri and E. Orfila, *Tratado de morfología y sistemática vegetal.* pp. 484, Ed. ACME. Buenos Aires, Argentina (1985).
2. A. Cassola, M. Latour, J. Pereyra and J. Serra, *Relevamiento expeditivo de recursos naturales de la zona cordillerana de la region Patagónica. Cap. IV: Relevamiento de vegetación.* EERA-INTA, 1-42 (1975).
3. M. Martínez Crovetto, *Apuntes sobre la vegetación de los alrededores del Lago Cholila.* Publicación Técnica N°1, 1-22, Facultad de Ciencias Agrarias. Universidad del Nordeste, Corrientes, Argentina (1980).
4. J.A. San Martin, *Medicinal plants in Central Chile.* Econ. Bot., **37**, 223 (1982).
5. G. Schemeda-Hirchsman et al., *La Farmacopea Mapuche, una fuente de productos biológicamente activos*, Revista Universum, Año 8, Universidad de Talca, Chile, 153-170 (1993).
6. P. Houghton and J. Manby, *Medicinal plants of the Mapuche.* J. Ethnopharm., 89-103 (1984).
7. G. Brown, *Phenylpropanoids and other secondary metabolites from Baccharis linearis.* Phytochemistry, **35**, 1037-1042 (1994).
8. K. He, G. Montenegro, J. Hoffmann and B. Timmermann, *Diterpenoids from Baccharis linearis.* Phytochemistry, **41**, 1123-1127 (1996).
9. C. Labbe, J. Rovirosa, F. Faini, M. Mahu, A. San Martín and M. Castillo. *Secondary metabolites fron Chilean Baccharis species.* J. Nat. Prod., **49**, 517-518 (1986).
10. G. Montes, F. Wilkomirski, R. Valenzuela and M. Neira, *Alkaloids of Baccharis linearis.* Rev. Real Acad. Cienc. Exactas Fis. Natur. Madrid, **65**, 499-511 (1971).
11. F. Faini, C. Labbe, and J. Coll, *Seasonal changes in chemical composition of epicuticular waxes from the leaves of Baccharis linearis.* Biochem. Syst. Ecol., **27**, 673-679 (1999).
12. F. Faini, F. Hellwig, C. Labbe and M. Castillo, *Hybridization in the genus Baccharis: Baccharis linearis x B. macraei.* Biochem. Syst. Ecol., **19**, 53-57 (1991).
13. V. Argandona and F. Faini, *Oleanolic acid content in Baccharis linearis and its effects on Heliothis zea larvae.* Phytochemistry, **33**, 1377-1379 (1993).
14. M. Sandoval, R. Valenzuela and F. Wilkomirski, *Determination of essential oils.* Fam. Nueva, **34**, 341-348 (1969).

Table I. Comparisons (%) of the leaf oils of *Baccharis racemosa* and *B. linearis*

Compound	RI	*Baccharis racemosa*	*Baccharis linearis* (A)	*Baccharis linearis* (B)
1-nonene	891	0.1	---	---
α-thujene	933	0.9	1.8	0.9
α-pinene	939	1.5	6.5	2.5
camphene	952	t	0.1	0.1
sabinene	975	13.6	---	---
β-pinene	980	2.8	14.9	6.5
myrcene	993	2.0	2.2	1.0
α-phellandrene	1004	0.4	0.2	0.1
δ-3-carene	1013	t	1.6	1.3
α-terpinene	1017	0.1	0.2	0.2
limonene	1032	13.3	27.6	27.8
(Z)-β-ocimene	1050	0.4	0.1	0.1
γ-terpinene	1062	0.4	1.2	0.4
cis-sabinene hydrate	1068	0.2	---	---
terpinolene	1089	0.6	0.8	0.2
linalool	1098	0.8	0.7	1.5
unknown 1	1112	---	0.1	0.1
cis-p-menth-2-en-1-ol	1121	---	0.1	0.1
isothujanol	1133	---	0.1	---
terpinen-4-ol	1176	1.2	1.6	1.1
α-terpineol	1189	0.3	0.8	0.8
unknown 2	1215	0.3	---	---
(E)-3-hexenyl isovalerate	1220	---	0.1	0.4
unknown 3	1277	---	0.1	---
trans-carvyl acetate	1337	0.2	---	---
α-cubebene	1351	---	0.1	0.3
neryl acetate	1366	---	0.1	t
α-copaene	1376	---	0.3	1.1
(E)-β-damascenone	1380	---	0.1	---
β-elemene	1393	0.6	0.4	0.8
α-gurjunene	1409	0.2	---	---
β-caryophyllene	1418	0.7	1.7	2.0
aromadendrene	1440	---	0.1	0.9
α-himachalene	1447	---	0.4	0.7
α-humulene	1454	1.0	0.9	1.6
9-epi-β-caryophyllene	1466	0.5	---	---
germacrene D	1480	---	1.6	4.7
unknown 4	1483	2.0	0.1	1.0
cis-β-guaiene	1490	0.9	---	---
viridiflorene	1493	---	0.9	t
bicyclogermacrene	1494	---	2.7	5.4
γ-cadinene	1515	---	0.4	1.5
unknown 5	1516	4.1	---	---
δ-cadinene	1524	5.3	3.9	6.7
cadina-1,4-diene	1533	---	0.1	0.5
α-cadinene	1538	---	0.1	1.0
α-calacorene	1544	0.9	0.1	1.0
unknown 6	1551	---	0.1	1.0
(E)-nerolidol	1564	5.0	---	---
ledol	1564	---	0.7	1.6
spathulenol	1576	0.5	1.5	0.8
caryophyllene oxide	1581	---	3.1	1.1
viridiflorol	1592	2.6	0.7	0.9
unknown 7	1616	6.5	---	---
unknown 8	1617	---	1.6	1.6
unknown 9	1618	1.8	---	---
unknown 10	1619	---	---	1.3
1-epi-cubenol	1627	---	1.6	1.9
cubenol	1643	---	4.7	6.0
α-muurolol	1645	9.7	1.6	1.1
α-cadinol	1655	3.1	4.5	3.0
unknown 11	1659	0.9	---	---
unknown 12	1664	---	1.2	t

Table I. Continued

Compound	RI	*Baccharis racemosa*	*Baccharis linearis* (A)	*Baccharis linearis* (B)
unknown 13	1672	0.4	---	---
occidentalol acetate	1680	0.1	---	---
unknown 14	1719	0.2	---	---
oplopanone	1733	0.2	---	---
aristolone	1757	0.2	---	---
unknown 15	1763	1.4	---	---
unknown 16	1782	0.6	---	---

RI: retention indices in DB-5; t = traces (< 0.1%)

Table II. Mass spectrum data of unknown components of *Baccharis racemosa* and *B. linearis* essential oils

RI-DB5	Compound	m/z (rel. int.)
1111	unknown 1	41(100), 69(96), 81(13), 13(11), 107(7), 135(6), 150(2)
1217	unknown 2	115(100), 108(86), 41(84), 83(82), 67(54), 55(41), 139(32)
1276	unknown 3	121(100), 43(63), 93(36), 136(22), 79(13), 105(12), 67(9)
1483	unknown 4	41(100), 150(50), 69(50), 81(43), 55(41), 93(36), 109(25)
1516	unknown 5	41(100), 81(52), 69(50), 81(43), 55(41), 93(36), 109(25)
1551	unknown 6	119(100), 41(82), 159(76), 105(67), 145(63), 91(44), 131(42)
1616	unknown 7	41(100), 97(54), 55(52), 79(49), 69(41), 107(29)
1617	unknown 8	43(100), 109(41), 69(38), 81(34), 55(32), 95(31), 122(29), 161(23)
1618	unknown 9	43(100), 162(38), 159(34), 91(20), 119(14), 105(11), 202(9)
1619	unknown 10	159(100), 41(79), 119(68), 105(61), 131(60), 91(32), 81(30)
1659	unknown 11	107(100), 81(84), 82(83), 121(43), 69(40), 55(36), 140(34)
1664	unknown 12	41(100), 91(50), 55(34), 105(36), 79(33), 119(23), 131(23), 159(23)
1672	unknown 13	41(100), 84(75), 81(56), 55(45), 109(32), 69(31), 161(34)
1719	unknown 14	43(100), 55(43), 71(32), 111(31), 223(18), 115(17), 83(15)
1763	unknown 15	43(100), 83(27), 55(23), 95(16), 119(15), 107(13), 159(11)
1782	unknown 16	57(100), 41(91), 43(89), 85(48), 69(59), 93(20), 159(18)

Table III. Group content of essential oils (%)

Group of compounds	*Baccharis racemosa*	*Baccharis linearis* (A)	*Baccharis linearis* (B)
Monoterpene hydrocarbons	36.0	57.2	41.1
Oxygenated monoterpenes	2.7	3.4	3.5
Sesquiterpene hydrocarbons	10.1	13.7	28.2
Oxygenated sesquiterpenes	21.4	18.4	16.4
Diterpene hydrocarbons	–	–	–
Oxygenated diterpenes	–	–	–

15. National Institute of Standards and Technology, *PC version of the NIST/EPA/NIH mass spectral database*. U.S. Department of Commerce, Gaithersburg, MD (1994).

16. R.P. Adams, *Identification of Essential Oil Components by Gas Chromatography/Mass Spectroscopy*. Allured Publ., Carol Steam, IL (1995).