J. Essent. Oil Res., **17**, 194-197 (March/April 2005)

Volatile Constituents of Leaf Oils from the Genus *Baccharis*. Part II: *Baccharis obovata* Hooker et Arnott and *B. salicifolia* (Ruiz et Pav.) Pers. Species from Argentina[a]

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 obovata* Hooker et Arnott and *B. salicifolia* (Ruiz et Pav.) Pers. leaves collected in the Argentinean Patagonia were isolated by steam distillation. Yields on the essential oils were 2.81% for *B. obovata* and 1.50% for *B. salicifolia*. The oils were analyzed by GC and GC/MS. The main constituents of each oil were: (i) *B. obovata* oil: α-thujene (5.8%), α-pinene (9.2%), sabinene (23.2%), β-pinene (9.9%), myrcene (3.7%), limonene (10.7%), terpinen-4-ol (5.9%); and (ii) *B. salicifolia* oil: α-thujene (2.1%), α-pinene (4.4%), sabinene (2.9%), β-pinene (5.5%), myrcene (2.2%), α-phellandrene (3.2%), limonene (8.1%), (Z)-β-ocimene (4.6%), terpinen-4-ol (5.9%), δ-cadinene (2.3%), elemol (2.7%), *cis*-α-copaen-8-ol (2.3%), α-muurolol (5.5%), α-eudesmol (2.7%), verboccidentafuran (2.8%), chromolaenin (3.1%) and dihydroisochromolaenin (2.9%).

Key Word Index

Baccharis obovata, *Baccharis salicifolia*, Asteraceae, essential oil composition, sabinene, β-pinene, limonene, α-muurolol, verboccidentafuran, chromolaenin, dihydroisochromolaenin.

Introduction

The genus *Baccharis* L. belongs to the Asteraceae family, Tubulifloroideae 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 grown distributed in all its territory. *Baccharis obovata* Hooker et Arno [= *B. umbelliformis* DC] (c.n. huautro) (Spanish) can be found from Parque Lanín to Los Alerces and *B. salicifolia* (Ruiz et Pav.) Pers. (n.v. chilca) (Spanish) can be found near Esquel city in the Argentinean Patagonia. *Baccharis obovata* and *B. salicifolia* mainly grow along the rivers, in humid places with a moderate climate (1-6).

There seems to be no previous work on the composition of *B. obovata*. Some studies have been reported on the secondary metabolites of *B. salicifolia* including phenolics, flavones, flavonoids and sterols (7-10). Two contributions have been reported on the oil composition of the leaves of *B. salicifolia* from Bolivia (11,12). No previous study on the composition of Argentinean *B. obovata* oil has been reported and only one on the composition of Argentinean *B. salicifolia* oil (13). The present study reports on the oil yields and the compositions of the leaf oils from the *B. ovovata* and *B. salicifolia* growing in Argentinean Patagonia.

Experimental

Sampling: Specimens were collected in spring from the following places: *B. obovata*: approx. 8 Km from Esquel city, La Hoya, Chubut Province, Argentina. *B. salicifolia*: Route 258, Km 3, Esquel city, Chubut Province, Argentina.

Voucher specimens have been deposited at the Herbarium of the Department of Forestal Botanics, Faculty of Engineering, National University of Patagonia, Chubut Province, Argentina.

[a]presented, in part, at the X Simposio Latinoamericano y VII Simposio Argentino de Farmacobotánica. Comodoro Rivadavia, Argentina, April 8-11, 2001.

*Address for correspondence

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

1041-2905/05/0002-0194$6.00/0—

Table I. Comparisons (percentage) of leaf oils of *Baccharis obovata* and *B. salicifolia*

Compound	RI	*Baccharis obovata*	*Baccharis salicifolia*	Compound	RI	*Baccharis obovata*	*Baccharis salicifolia*
(E)-3-hexenol	857	0.2	-	γ-muurolene	1477	0.1	1.1
unknown 1	868	0.9	-	germacrene D	1480	0.6	1.4
1-nonene	891	0.3	-	β-selinene	1485	-	1.1
α-thujene	931	5.8	2.1	bicyclogermacrene	1494	0.7	-
α-pinene	939	9.2	4.4	unknown 11	1511	-	1.1
camphene	953	0.1	-	γ-cadinene	1513	t	1.2
sabinene	976	23.2	2.9	δ-cadinene	1524	0.6	2.3
β-pinene	980	9.9	5.5	unknown 12	1528	0.2	-
myrcene	991	3.7	2.2	β-cadinene	1530	-	0.6
α-phellandrene	1005	0.1	3.2	*trans*-calamenene	1532	-	0.7
δ-3-carene	1011	t	-	α-calacorene	1542	-	1.9
α-terpinene	1018	1.8	0.5	tricyclo[4.4.0.0.2,7]dec-8-ene 3 methanol α,α,6,8 tetramethyl* [1]	1546	0.1	-
p-cymene	1026	-	0.9	elemol	1549	-	2.7
limonene	1031	10.7	8.1	*cis*-α-copaen-8-ol	1555	-	2.3
(Z)-β-ocimene	1050	0.1	4.6	(E)-nerolidol	1564	0.4	-
γ-terpinene	1062	3.1	1.1	ledol	1565	t	-
cis-sabinene hydrate	1068	0.2	0.1	germacrene D-4-ol	1568	-	0.2
terpinolene	1088	0.8	1.9	spathulenol	1576	1.4	-
linalool	1098	0.4	0.6	caryophyllene oxide	1581	1.1	0.8
unknown 2	1111	0.1	-	globulol	1583	0.2	-
cis-p-menth-2-en-1-ol	1121	0.4	-	guaien-4-ol	1616	-	0.3
isothujyl alcohol	1133	0.8	-	unknown 13	1617	-	0.3
trans-limonene oxide	1139	0.3	-	10-epi-γ-eudesmol	1619	0.1	-
pinocarvone	1162	0.2	-	1-epi-cubenol	1627	0.2	-
unknown 3	1175	0.1	-	hinesol	1638	-	1.8
terpinen-4-ol	1177	5.9	1.9	epi-α-muurolol	1641	0.4	-
α-terpineol	1189	0.5	0.4	α-muurolol	1645	0.3	5.5
myrtenal	1193	0.4	-	α-eudesmol	1653	-	2.7
trans-piperitol	1205	0.1	-	α-cadinol	1653	1.2	-
(Z)-3-hexenyl isovalerate	1220	-	0.2	unknown 14	1659	0.5	-
unknown 4	1256	1.6	-	verboccidentafuran* [2]	1662	-	2.8
unknown 5	1269	0.5	-	unknown 15	1672	1.1	-
unknown 6	1272	-	0.2	unknown 16	1674	0.2	-
unknown 7	1276	0.4	-	unknown 17	1682	0.5	-
unknown 8	1280	-	0.4	α-bisabolol	1683	-	1.9
cis-verbenyl acetate	1282	0.2	-	unknown 18	1687	-	1.0
safrole	1285	-	1.7	14-hydroxy-α-humulene	1709	0.2	-
trans-sabinyl acetate	1291	t	-	cromolaenin* [3]	1726	-	3.1
unknown 9	1292	-	1.1	unknown 19	1741	-	1.8
cis-pinocarvyl acetate	1309	0.1	-	dihydroisochromolaenin* [4]	1763	-	2.9
α-terpinyl acetate	1350	0.6	-	8-α-acetoxielemol	1789	-	0.6
cis-carvyl acetate	1362	0.9	-	unknown 20	1818	0.6	-
neryl acetate	1365	t	-	unknown 21	1872	-	0.9
unknown 10	1371	0.1	-	unknown 22	1900	-	0.9
α-copaene	1376	t	-	unknown 23	1938	-	1.8
sativene	1388	-	0.6	unknown 24	2040	-	0.5
β-elemene	1391	0.5	-	unknown 25	2083	-	0.7
methyl eugenol	1401	-	0.6	unknown 26	2090	-	0.9
β-caryophyllene	1418	0.4	0.9				
α-humulene	1454	0.2	0.1				
(E)-β-farnesene	1458	-	0.9				

RI = retention indices in DB5; t = traces (< 0.1%); *tentative identification; [1] m/z 59(100), 162(57), 105(45), 119(39), 132(37), 147(33), 187(9); [2] m/z 216[M]+(77), 201(100), 157(52), 145(27), 115(23), 91(23), 173(18), 131(16); [3] m/z 212[M+](100), 197(96), 169(41), 152(39), 182(38), 141(22), 91(38); [4] m/z 214[M+](100), 199(45), 159(32), 129(31), 115(30), 171(29), 143(29)

Oil isolation: The oil was obtained by water distillation for 3 h using a Clevenger-type apparatus. The samples were subjected to five replicates giving an average yield (mL of oil per 100 g of extracted leaves) of 2.81% (standard deviation 0.02%) for *B. obovata*; and 1.50% (standard deviation 0.03%) for *B. salicifolia*.

Component identifications: 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

Table II. Mass spectral data of unknown components of *Baccharis obovata* and *B. salicifolia* oils

RI	Compound	m/z (rel. int.)
868	unknown 1	122 [M]$^+$(11), 79(100), 107(50), 39(41), 93(36), 91(35), 66(19)
1111	unknown 2	41(100), 69(96), 81(13), 13(11), 107(7), 135(6), 150(2)
1175	unknown 3	107(100), 41(95), 122(82), 79(80), 57(80), 69(40), 93(18)
1256	unknown 4	41(100), 43(95), 83(91), 108(90), 67(64), 55(45), 139(32)
1269	unknown 5	100(100), 41(82), 69(60), 81(41), 122(36), 123(35), 55(27), 150(9)
1272	unknown 6	79(100), 41(57), 91(50), 39(48), 105(23), 53(22), 67(18)
1276	unknown 7	121(100), 43(63), 93(36), 136(22), 79(13), 105(12), 67(9)
1280	unknown 8	43(100), 95(41), 93(32), 41(30), 121(21), 136(20), 108(14)
1292	unknown 9	194 M$^+$ (2), 179(100), 43(84), 41(82), 69(73), 55(43), 107(28), 95(22)
1371	unknown 10	43(100), 93(68), 121(45), 67(36), 107(22), 136(18), 79(15)
1511	unknown 11	105(100), 43(73), 41(59), 119(45), 93(36), 81(27), 55(23)
1528	unknown 12	43(100), 95(64), 81(63), 109(54), 55(39), 124(32), 137(31)
1617	unknown 13	41(100), 109(88), 95(87), 43(83), 161(63), 119(40), 55(39)
1659	unknown 14	41(100), 93(52), 67(39), 79(38), 55(37), 107(32), 131(25)
1672	unknown 15	43(100), 93(66), 55(39), 79(36), 119(34), 105(34), 69(34), 205(25)
1674	unknown 16	41(100), 109(66), 43(65), 91(57), 159(45), 79(44), 55(41)
1682	unknown 17	84(100), 41(86), 55(45), 69(39), 161(33), 105(32), 121(27)
1687	unknown 18	41(100), 159(49), 91(48), 55(47), 79(46), 119(44), 55(41)
1741	unknown 19	199(100), 214(90), 115(44), 128(41), 43(36), 142(35), 157(30)
1818	unknown 20	43(100), 68(95), 57(73), 95(68), 82(63), 123(39), 109(19)
1872	unknown 21	43(100), 109(38), 81(34), 95(27), 55(26), 69(20), 123(15)
1900	unknown 22	210(100), 165(41), 195(32), 152(18), 104(15), 76(14), 181(8)
1938	unknown 23	197(100), 230(73), 43(63), 169(50), 91(49), 115(47), 128(45)
2040	unknown 24	173(100), 145(57), 216(43), 115(32), 188(30), 159(18), 91(18)
2083	unknown 25	228(100), 213(75), 198(48), 185(34), 115(27), 141(25), 99(22)
2090	unknown 26	43(100), 71(100), 41(82), 57(54), 55(53), 81(48), 95(40)

checked with the retention time of a pure standard compound on two columns of different polarity. Peak area percentages were calculated without using either correction factors or an internal standard. The mass spectra were compared to spectra already reported in the literature (14,15) 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 obovata yielded 2.81% of a pale yellow liquid (Specific gravity 0.865; Refractive index 1.4434 at 20°C) with a herbaceous-citric aroma. *Baccharis salicifolia* yielded 1.50% of a pale yellow liquid (Specific gravity 0.71; Refractive index 1.4621 at 20°C) with a citric odor.

Table I summarizes the qualitative and quantitative analyses of these two leaf oils. For *B. obovata*, the main constituents were α-thujene (5.8%), α-pinene (9.2%), sabinene (23.2%), β-pinene (9.9%), myrcene (3.7%), limonene (10.7%), terpinen-4-ol (5.9%). For *B. salicifolia*, the main constituents were α-thujene (2.1%), α-pinene (4.4%), sabinene (2.9%), β-pinene (5.5%), myrcene (2.2%), α-phellandrene (3.2%), limonene (8.1%), (Z)-β-ocimene (4.6%), terpinolene (1.9%), terpinen-4-ol (5.9%), δ-cadinene (2.3%), α-calacorene (1.9%), elemol (2.7%), *cis*-α-copaen-8-ol (2.3%), hinesol (1.8%), α-muurolol (5.5%), α-eudesmol (2.7%), verboccidentafuran (2.8%), α-bisabolol (1.9%), chromolaenin (3.1%) and dihydroisochromolaenin (2.9%).

Table II shows the mass spectrum data of unknown components of *B. racemosa* and *B. linearis* essential oils. Table III shows the variation in group contents of the leaf oils from the three species under study. *Baccharis obovata* oil was richer in monoterpene hydrocarbons (about 68.5%). Significant amounts of oxygenated monoterpenes, but no sesquiterpene hydrocarbons or oxygenated sesquiterpenes, were found in the *B. obovata* oil. *Baccharis salicifolia* oil was richer in monoterpene

Table III. Group content of essential oils (percentage)

Group of compounds	*Baccharis obovata*	*Baccharis salicifolia*
Monoterpene hydrocarbons	68.5	37.4
Oxygenated monoterpenes	11.0	3.0
Sesquiterpene hydrocarbons	3.1	12.8
Oxygenated sesquiterpenes	5.5	27.6
Diterpene hydrocarbons	-	-
Oxygenated diterpenes	-	-

hydrocarbons and oxygenated sesquiterpenes. Neither diterpene hydrocarbons nor oxygenated diterpenes were found in *B. obovata* or *B. salicifolia* 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.* 484 pp. 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.* 1-42, EERA-INTA (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 Martín, *Medicinal plants in Central Chile.* Econ. Bot., **37**, 216-227 (1982).
5. G. Schemeda-Hirchsman et al., *La Farmacopea Mapuche, una fuente de productos biológicamente activos.* Revista Universum, **8**, 153-170, Universidad de Talca, Chile (1993).
6. P. Houghton and J. Manby, *Medicinal plants of the Mapuche.* J. Etnopharmacol., 89-103 (1984).
7. E. Wollenweber, F. Arriaga-Giner, A. Rumbero and W. Greenaway, *New phenolics from Baccharis leaf exudate.* Z. Naturforsch., C: Biosci., **44**, 727-730 (1989).
8. U. Warning, F. Bohlmann, V. Sanchez, S. Del Río and X. Dominguez, *New constituents of Baccharis salicifolia.* Rev. Latinoam. Quim., **17**, 199-200 (1986).
9. J. Kavka, E. Guerreiro, O. Giordano and J. Romo, *Flavonoids of Baccharis salicifolia.* Rev. Latinoam. Quím., **4**, 101-104 (1973).
10. X. Domlinguez, H. Sánchez, B. Merijanian, M. Rojas and C. Paulino, *Stigmasterol, friedooleanan-3b-ol and Baccharis oxide from Baccharis salicifolia.* Phytochemistry, **11**, 2628 (1972).
11. I. Loayza, G. Collin, M. Gagnon and E. Dellacassa, *The essential oils of Baccharis Latifolia, B. salicifolia from Bolivia, and B. dracunculifolia from Uruguay.* Rivista Ital. EPPOS, **4**, 728-736 (1993).
12. I. Loayza, D. Abujder, R. Aranda, J. Jakupovic, G. Collin, H. Deslauriers and F.I. Jean, *Essential oils of Baccharis salicifolia, B. latifolia and B. dracunculifolia.* Phytochemistry, **38**, 381-389 (1985).
13. M. Zunino, M. Novillo-Newton, D. Maestri and J. Zygadlo, *Composition of the essential oil of Baccharis crispa Spreng. and B. salicifolia Pers. grown in Córdoba (Argentina).* Flav. Fragr. J., **12**, 405-407 (1997).
14. National Institute of Standards and Technology, *PC version of the NIST/EPA/NIH mass spectral database.* U.S. Department of Commerce, Gaithersburg, MD (1994).
15. R.P. Adams, *Identification of Essential Oil Components by Gas Chromatography/Mass Spectroscopy.* Allured Publ., Carol Steam, IL (1995).