6. C.O. Okoli, P.A. Akah, S.V. Nwafor, A.I. Anisiobi, I.N. Ibegbunam and O. Erojikwe, *Anti-inflammatory Activity of Hexane Extracts and of* Aspilia africana *C. D. Adams.* J. Ethnopharmacol., **109**, 219–225 (2007).
7. J.-R. Kuiate, P.-H. Amvam Zollo, G. Lamaty, C. Menut and J.-M. Bessière, *Composition of the Essential Oils From the Leaves of Two Varieties of* Aspilia africana *(Pers.) C. D. Adams From Cameroon.* Flav. Fragr. J., **14**, 167–169 (1999).
8. R.P. Adams, *Identification of Essential Oil Components by Gas Chromatography/Mass Spectroscopy*. Allured Publ. Corp., Carol Stream, IL (2001).
9. O.A. Oyedeji and A.J. Afolayan, *Chemical Composition and Antibacterial Activity of the Essential Oil of* Centella asiatica *Growing in South Africa.* Pharm. Biol., **43**, 249–252 (2005).
10. N.J. Manenzhe, N. Potgieter and T. van Ree, *Composition and Antimicrobial Activities of Volatile Components of* Lippia javanica*.* Phytochemistry, **65**, 2333–2336 (2004).
11. O.R. Omobuwajo, A.A. Gbolade, R. Nia and F.B. Adewoyin, *Constituents and Insecticidal Activities of Essential Oil in* Citrus sinensis *Fruit Peel*. J. Trop. Med. Plants, **6**, 265–270 (2005).

Composition of Essential Oils From Five Aromatic Species of Asteraceae

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Abstract

The chemical composition of essential oils of five aromatic Asteraceae native of Chile was examined using GC and GC/MS. In the oil of *Gnaphalium philippi* Cabrera, 25 compounds were identified, with (E)-nerolidol (44.3%) and dodecanoic acid (8.7%) predominating. Seventeen compounds were identified in the oil of *Leptocarpha rivularis* DC., with caryophyllene oxide (25.2%), β-caryophyllene (21.1%), and α-thujone (11.9%) being the major ones. In the oil of *Ophryosporus pinifolius* (Phil.) King et H. Robinson, 23 compounds were identified, with limonene (35.9%) and β-caryophyllene (9.4%) being the major constituents. Eleven compounds were identified in the oil of *Senecio adenotrichius* DC., dehydrofukinone (70.9%) being the major one. In the oil of *Senecio zoellneri* Martic. et Quez., 21 compounds were identified, the predominant ones being δ-3-carene (19.5%), β-phellandrene (18.0%), β-pinene (16.4%), and α-pinene (10.8%). Monoterpenes predominated in *O. pinifolius* and *S. zoellneri*, and sesquiterpenes predominated in *G. philippi*, *L. rivularis*, and *S. adenotrichius*.

Key Word Index

Gnaphalium philippi, *Leptocarpha rivularis*, *Ophryosporus pinifolius*, *Senecio adenotrichius*, *Senecio zoellneri*, Asteraceae, essential oil composition, dehydrofukinone, caryophyllene oxide, dodecanoic acid, (E)-nerolidol, β-caryophyllene, α-thujone, β-phellandrene, limonene, δ-3-carene, β-pinene, α-pinene.

Introduction

Chile is a narrow and long country; it spans almost 38° of latitude but has an average width of only *ca.* 200 km. It has an ample variety of biogeographical zones (1), and is endowed with a rich flora with a high degree of endemism attributed to the isolation provided by the desert in the North, the Andes range in the East, and the Pacific Ocean in the West (2). Most chemical work on native species of the flora has been performed in search for compounds with pharmacological activity (3), and little emphasis has been given to the search of aromatic plant species and to their chemical constituents. In this paper we describe the composition of the essential oils from five species which have been collected from widely different biogeographical zones: *Ophryosporus pinifolius* (Phil.) R.M. King et H.

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Robinson from the desertic Andes in the northernmost part of the country, *Senecio zoellneri* Martic. et Quez. from the high-mountain plateau in the northeast corner of the country, *Gnaphalium philippi* Cabrera and the endemic species *Senecio adenotrichius* DC. from the sclerophyllous forests in the center of the country, and the endemic species *Leptocarpha rivularis* DC., from the Southern temperate rain forests. In the field, the aerial tissues of all these species exhibit attractive aromas which intensify upon crushing of the tissues, suggesting the occurrence of aromatic oils.

Experimental

Plant material: Samples of aboveground tissue were collected at different localities in Chile, as follows: *G. philippi* (Ocoa, 32°54.7S, 71°03.4W, 477 masl), *L. rivularis* (Valdivia, 39°52.4S, 73°14.6W, 4 masl), *O. pinifolius* (Cuesta Cardones, 18°27.4S, 69°46.6W, 2378 masl), *S. adenotrichius* (Ocoa, 32°54.7S, 71°02.4W, 506 masl), and *S. zoellneri* (Portezuelo de Chapiquiña, 18°19.9S, 69°30.5W, 4395 masl). All samples were collected during the flowering season. The material was identified by Sebastian Teillier, Universidad Central de Chile. Voucher specimens are stored at the Herbarium of Universidad de Concepción (CONC).

Oil isolation and analysis: Plant material was air dried, cut into small pieces, and submitted to hydrodistillation for 3 h using a modified Clevenger-type apparatus. Oils were dried over anhydrous sodium sulphate and stored in glass ampoules at 4°C until analyzed. All oils were yellowish.

Table I. Chemical composition (%) of the essential oils of *Gnaphalium philippi, Leptocarpha rivularis, Ophryosporus pinifolius, Senecio adenotrichius*, and *Senecio zoellneri*

Compound	RI [a]	Concentration (%) [b]					Identification [c]
		Gnaphalium philippi	*Leptocarpha rivularis*	*Ophryosporus pinifolius*	*Senecio adenotrichius*	*Senecio zoellneri*	
α-thujene	930	- [d]	-	4.8	-	0.9	MS,RI
α-pinene	937	1.7	-	3.3	2.5	10.8	MS,RI,ST
sabinene	974	-	-	7.3	-	3.4	MS,RI
β-pinene	977	-	-	5.9	-	16.4	MS,RI,ST
β-myrcene	990	-	-	1.3	-	0.8	MS,RI,ST
α-phellandrene	1003	-	-	0.5	-	2.7	MS,RI,ST
δ-3-carene	1010	-	-	-	-	19.5	MS,RI,ST
α-terpinene	1019	-	-	1.2	4.5	1.7	MS,RI,ST
o-cymene	1024	-	-	0.5	-	2.7	MS,RI
p-cymene	1026	-	-	-	-	2.9	MS,RI,ST
limonene	1030	0.1	-	35.9	-	-	MS,RI,ST
β-phellandrene	1031	-	-	-	-	18.0	MS,RI
1,8-cineole	1033	0.8	-	-	-	-	MS,RI
(Z)-β-ocimene	1039	-	-	-	-	3.4	MS,RI
phenylacetaldehyde	1041	0.1	-	-	-	-	MS,RI,ST
(E)-β-ocimene	1050	-	-	2.1	5.8	0.6	MS,RI
γ-terpinene	1059	0.1	-	2.9	-	2.9	MS,RI,ST
terpinolene	1088	-	-	1.8	-	3.7	MS,RI
isoterpinolene	1088	0.1	-	-	-	-	MS,RI
linalool	1101	0.1	1.5	-	-	-	MS,RI,ST
α-thujone	1108	0.3	11.9	-	-	-	MS,RI,ST
β-thujone	1120	-	0.6	-	-	1.4	MS,RI,ST
allo-ocimene*	1129	-	-	-	-	1.5	MS,RI
verbenol	1153	-	0.9	-	-	-	MS,RI
terpinen-4-ol	1179	0.4	0.8	2.5	-	2.7	MS,RI
cryptone	1189	-	-	-	-	0.2	MS,RI
α-terpineol	1191	1.1	-	-	-	-	MS,RI,ST
(Z)-3-hexenyl-2-methylbutyrate	1230	0.1	-	-	-	-	MS,RI
nonanoic acid	1277	1.0	-	-	-	-	MS,RI
sabinyl acetate	1298	-	5.5	-	-	-	MS,RI
1,5,5-trimethyl-6-methylene-cyclohexene	1339	-	-	0.3	-	-	MS,RI
α-longipinene	1360	-	2.3	-	-	-	MS,RI,ST
decanoic acid	1378	1.1	-	-	-	-	MS,RI
β-bourbonene	1397	-	0.5	-	-	-	MS,RI
β-elemene	1398	-	-	0.3	1.3	-	MS,RI
methyl eugenol	1401	-	-	1.0	-	-	MS,RI,ST
β-cubebene	1403	-	4.0	-	-	-	MS,RI
β-bergamotene*	1420	3.2	-	-	-	-	MS,RI
β-caryophyllene	1436	-	21.1	9.4	1.3	-	MS,RI,ST
β-gurjunene	1441	-	1.5	-	-	-	MS,RI

Table I. Continued

Compound	RI [a]	Concentration (%) [b]					Identification [c]
		Gnaphalium philippi	*Leptocarpha rivularis*	*Ophryosporus pinifolius*	*Senecio adenotrichius*	*Senecio zoellneri*	
α-bergamotene*	1442	2.1	-	-	-	-	MS,RI
(E)-β-farnesene	1456	2.0	-	-	-	-	MS,RI
α-humulene	1468	-	2.5	0.6	-	-	MS,RI,ST
undecanoic acid	1471	0.8	-	-	-	-	MS,RI
ar-curcumene	1486	1.0	-	-	-	-	MS,RI
longifolene	1487	-	-	-	0.6	-	MS,RI,ST
γ-muurolene	1489	-	0.6	-	-	-	MS,RI
germacrene D	1492	-	9.3	1.6	1.0	-	MS,RI
β-selinene	1496	-	-	0.7	-	-	MS,RI
ledene	1503	-	-	1.4	1.3	-	MS,RI
(E,E)-α-farnesene	1508	1.1	-	-	-	-	MS,RI
γ-cadinene	1510	-	2.1	-	-	-	MS,RI
germacrene B	1511	-	-	-	0.9	0.4	MS,RI
β-bisabolene	1512	2.2	-	-	-	-	MS,RI
δ-cadinene	1536	-	1.4	0.6	-	0.2	MS,RI
(E)-nerolidol	1569	44.3	-	0.3	-	-	MS,RI
dodecanoic acid	1585	8.7	-	-	-	-	MS,RI
spathulenol	1595	-	-	-	1.2	-	MS,RI
caryophyllene oxide	1603	-	25.2	-	-	-	MS,RI,ST
tridecanoic acid	1666	1.4	-	-	-	-	MS,RI
α-bisabolol	1689	2.7	-	-	-	-	MS,RI
tetradecanoic acid	1764	1.5	-	-	-	-	MS,RI
dehydrofukinone	1832	-	-	-	70.9	-	MS,RI
Monoterpene hydrocarbons (%)		2.1	-	67.5	12.9	92.1	
Oxygenated monoterpenes (%)		2.8	21.3	2.5	-	4.3	
Sesquiterpene hydrocarbons (%)		11.5	45.2	14.6	6.4	0.7	
Oxygenated sesquiterpenes (%)		47.0	25.2	0.3	72.1	-	
Other compounds (%)		14.6	-	1.3	-	-	
Total identified (%)		77.9	91.7	86.2	91.3	97.0	
Oil yield (mL/100 g dry weight)		0.12	0.27	0.15	0.36	0.41	

[a] Retention indexes on an SPB-5 column in reference to n-alkanes; [b] Peak areas relative to total peak area; [c] -, not detected; [d] MS, NIST MS library, and the literature; RI, retention index; ST, authentic standard compound; * correct isomer not identified.

Qualitative analyses were performed in a Hewlett-Packard 5891 gas chromatograph linked to a Hewlett-Packard 5972 mass spectrometric detector with an integrated data system (Hewlett-Packard, Palo Alto, CA, USA), and quantitative analyses were performed in a Shimadzu GC-9A gas chromatograph fitted with a FID-9 detector (Shimadzu Corporation, Kyoto, Japan). The same capillary column (SPB-5, film thickness 0.25 µm, 30 m × 0.25 mm, Supelco, Deerfield, IL, USA) was used in both instruments. The operating conditions were as follows: on-column injection; injector temperature, 150°C; detector temperature, 280°C; carrier gas, He; oven temperature program: 50°C for 10 min, increase to 280°C at 5°C/min, and then 280°C for 45 min. In the mass detector, ionization was by electron impact at 70 eV; scan time, 1.5 s; and acquisition mass range, 50–500 amu. The identification of compounds in the chromatographic profiles was achieved by i) comparison of mass spectra with those in the NIST98 library database using a reverse search technique which verifies that main peaks in the reference spectrum are present in the unknown spectrum (4), and ii) comparison of retention indexes (RI) with those reported in the literature or with those of available standards. Quantitation was achieved by integration of peak areas in the chromatogram from the FID-fitted gas chromatograph.

Results and Discussion

Table I shows the compositions and contents of individual components of the oils of the five species studied, as well as their respective yields. From the oil of *G. philippi* 25 compounds were characterized, among them a series of straight chain carboxylic acids (C_9 to C_{14}) amounting to 14.3% of the total peak area, monoterpenes (4.9%), and also sesquiterpenes (58.5%), the most abundant of which was (E)-nerolidol (44.3%).

The oil of *L. rivularis* consisted solely of terpenes, most of which were sesquiterpene hydrocarbons (45.2%), among them β-caryophyllene (21.1%) and germacrene D (9.3%). Oxygenated terpenes accounted for the remaining terpenes (46.5%), with caryophyllene oxide (25.2%) and α-thujone (11.9%) being the major compounds in this group. Previous work on extracts of *L. rivularis* has shown the presence of sesquiterpene lactones of the heliangolide type (5–7).

The oil of *O. pinifolius* consisted almost exclusively of terpene hydrocarbons (82.1%), most of which were monoterpenes (67.5%), mainly limonene (35.9%) and sabinene (7.3%). To the best of our knowledge, no previous chemical studies are available on this species.

The oil of *S. adenotrichius* contained a surprisingly high amount of dehydrofukinone (70.9%). This sesquiterpene has been found as main constituent (21%) of the oil of *Senecio glaucus* subsp. *coronopifolius* (8), and has also been isolated from agarwood (*Aquilaria agallocha*; Thymelaeceae) oil (9). Studies of the resinous exudates of *S. adenotrichius* have yielded phenols, aromatic and aliphatic acids, sesquiterpenes, and indole (10).

Monoterpene hydrocarbons were the main constituents of the oil of *S. zoellneri* (92.1%), major ones being δ-3-carene (19.5%), β-phellandrene (18.0%), β-pinene (16.4%), and α-pinene (10.8%). Previous work on extracts of *S. zoellneri* showed the presence of oxygenated furoeremophilane derivatives and seco-furoeremophilanolides (11).

Interestingly, the oils of species thriving at relatively low altitudes (*G. philippi*, *L. rivularis* and *S. adenotrichius*) contained predominantly oxygenated terpenes (49.8%, 46.5% and 72.1%, respectively), while the two species which grow at high altitudes (*O. pinifolius* and *S. zoellneri*) contained mostly terpene hydrocarbons (82.1% and 92.7%, respectively).

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References

1. R. Gajardo, *La vegetación natural de Chile. Clasificación y distribución geográfica*. Editorial Universitaria: Santiago, Chile (1994).
2. J.A. Simonetti, M.T.K. Arroyo, A.E. Spotorno and E. Lozada, *Diversidad biológica en Chile*. Comisión Nacional de Ciencia y Tecnología: Santiago, Chile (1995).
3. H.M. Niemeyer, *Biologically Active Compounds From Chilean Medicinal Plants*. In: *Recent Advances in Phytochemistry. Vol. 29, Phytochemistry of Medicinal Plants*. Edits., J.T. Arnason, R. Matta and J.T. Romeo, pp. 137–159, Plenum Press, New York , NY (1995).
4. G.M. Pesyna, R. Ventakaraghavan, H.E. Dayringer and F.W. McLafferty, *Probability Based Matching System Using a Large Collection of Reference Mass-spectra*. Anal. Chem., **48**, 1362–1368 (1976).
5. R. Martínez, V. Kesternich, H. Carrasco, C. Bustos and S. Fernández, *Structure, Conformation and Biological Activity Studies on Rivularin, a New Heliangolide Isolated From* Leptocarpha rivularis. Bol. Soc. Chil. Quim., **43**, 7–12 (1998).
6. R. Martínez, V. Kesternich, E. Gutiérrez, H. Dolz and H. Mansilla, *Conformational Analysis and Biological Activity of Leptocarpin and Leptocarpin Acetate*. Planta Med., **61**, 188–189 (1995).
7. R. Martínez, I.S. Ayamante, J.A. Núñez-Alarcón and A. Romo de Vivar, *Leptocarpin and 17,18-Dihydroleptocarpin, 2 New Heliangolides From* Leptocarpha rivularis. Phytochemistry, **18**, 1527–1528 (1979).
8. H.L. De Pooter, L.F. De Buyck, N.M. Schamp, E. Aboutabl, A. De Bruyn and S.Z. Husain, *The Volatile Fraction of* Senecio glaucus *subsp.* coronopifolius. Flav. Fragr. J., **1**, 159–163 (1986).
9. H.Z. Alkhathlan, H.M. Al-Hazimi, F.S. Al-Dhalaan and A.A. Mousa, *Three 2-(2-phenylethyl) Chromones and Two Terpenes From Agarwood*. Nat. Prod. Res., **19**, 367–372 (2005).
10. A. Urzúa and L. Andrade, *Comparative Chemical Composition of the Resinous Exudates From* Senecio adenotrichius *and* S. viscosissimus. Biochem. Syst. Ecol., **29**, 865–867 (2001).
11. M. Ahmed, J. Jakupovic, F. Bohlmann and H.M. Niemeyer, *Highly Oxygenated Furoeremophilane Derivatives From* Senecio zoellneri. Phytochemistry, **30**, 2407–2409 (1991).