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Aromatic plants of northwest Argentina. Constituents of the essential oils of aerial parts of seven Verbenaceae: Lantana and Aloysia.

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Abstract

The chemical composition of essential oil samples of the aerial parts of *Lantana canescens*, *Lantana tilcarensis*, *Lantana trifolia*, *Aloysia citriodora*, *Aloysia gratissima*, *Aloysia castellanosii* and *Aloysia catamarcensis* from northwest Argentina, phytogeographic areas of Yungas, Puna, Parque Chaqueño and Monte, have been analyzed by GC and GC/MS. The main oil component group present in the oils of the aerial parts of *Lantana* species were sesquiterpene hydrocarbons (> 24.8%). In contrast, the main compound group found in the oils of *Aloysia* species were oxygenated monoterpenes (> 19.6%). The comparison with previous studies performed by other authors points to a significant variation in the chemical composition of essential oil depending on the origin of the plants.

Key Word Index

Lantana canescens, Lantana tilcarensis, *Lantana trifolia*, *Aloysia citriodora*, *Aloysia gratissima, Aloysia castellanosii*, *Aloysia catamarcensis*; *Verbenaceae* essential oil composition. Sarbinene, 1,8-cineole, α-thujone, carvone, geranial, thymol, geranyl acetate, β-elemene, (Z)- β-farnesene, α-humulene, germacrene D, (E)- β-farnesene, γ-cadenene, spathulenol, α-muurolol.

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Introduction

The present research study was carried out in the phytogeographic areas of Yungas, Puna, Parque Chaqueño and Monte (1). In these areas, the leaves of *Lantana canescens* Kunth, *Lantana tilcarensis* Tronc., *Lantana trifolia* L., *Aloysia citriodora* Ortega ex Pers., hom. illeg., *Aloysia gratissima* (Gillies et Hook. ex Hook.) Tronc., *Aloysia castellanosii* Moldenke and *Aloysia catamarcensis* Moldenke are largely used in herbal teas for their aromatic, digestive and antispasmodic properties (2-7). *Aloysia* and *Lantana* (Verbenaceae) are genera of aromatic shrubs comprising about 40 and 150 species, respectively, disseminated mainly in tropical and subtropical regions of the Americas (6,7). These genera are difficult to classify taxonomically since their species are not stable and hybridization is widespread (8). Moreover, some species of *Lantana* or *Aloysia* have been considered as species of *Lippia* (Verbenaceae), because both

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Table I. Vouchers of species analyzed

Species	Locality	Altitude (m)	Collector
1) *Lantana canescens* Kunth	Jujuy. Dpto. Ledesma. Parque Nacional Calilegua. Phytogeographic area: Yungas		Rotman- 1374 (JUA)
2) *Lantana canescens* Kunth	Jujuy. Dpto. Dr. Manuel Belgrano. Localidad Chijra. Phytogeographic area: Yungas.	1270	Rotman- 1336 (JUA)
3) *Lantana tilcarensis* Tronc.	Jujuy. Dpto. Tumbaya. Localidad Volcán-Laguna. Phytogeographic area: Monte		Rotman- 1380 (JUA)
4) *Lantana trifolia* L.	Jujuy. Dpto. Dr. Manuel Belgrano. Localidad Chijra. Phytogeographic area: Yungas.	1270	Rotman- 1337 (JUA)
5) *Aloysia citriodora* Ortega ex Pers., hom. illeg.	Jujuy. Dpto. Tumbaya. Localidad Volcán-Laguna. Phytogeographic area: Puna		Rotman- 1379 (JUA)
6) *Aloysia citriodora* Ortega ex Pers., hom. illeg.	La Rioja. Dpto. Sanagasta. Sierra de Velasco, quebrada Orcollorcán. Phytogeographic area: Parque Chaqueño.	1770	Biurrun et al. 7732 (IZAC)
7) *Aloysia gratissima* (Gillies et Hook. ex Hook.) Tronc..	La Rioja. Dpto. Chamical. Campo Experimental Las Vizcacheras (INTA). Phytogeographic area: Parque Chaqueño.	425	Biurrun et al. 8757 (CHAM)
8) *Aloysia castellanosii* Moldenke	La Rioja. Dto. Cnel. Felipe Varela. Parque Nacional Talampaya. Sierra de Los Tarjados, cañón de Talampaya: sector “Los Cajones” Phytogeographic area: Monte.	1730	Biurrun et al. - 7915 (IZAC)
9) *Aloysia catamarcensis* Moldenke	La Rioja. Dto. Independencia. Río Carrizal. Entre Cerro Peinado y Sierra de Vilgo. Phytogeographic area: Monte	1375	Biurrun et al. - 7889 (IZAC)

Table II. Percentage composition of the essential oils of *Lantana canescens* (Lc1,Lc2), *Lantana tilcarensis* (Lti), *Lantana trifolia* (Ltr), *Aloysia citriodora* (Aci5, Aci6), *Aloysia gratissima* (Ag), *Aloysia castellanosii* (Acas) and *Aloysia catamarcensis* (Acat)

RI	RI										
Supelcowax 10	**DB-5**	**Compounds[a,c]**	**Lc1**	**Lc2**	**Lti**	**Ltr**	**Aci5**	**Aci6**	**Ag**	**Acas**	**Acat**
	930	α-thujene						0.4		t	
	939	α-pinene [b]	t	t				t	3.1		t
	954	camphene						0.2			
	975	sabinene [b]	t	t					8.3	44.8	
	979	β-pinene [b]						1.7	1.1		
	991	myrcene [b]								t	
	1025	p-cymene [b]	t	t					2.2	0.5	
	1028	limonene	0.6	0.3	0.2	0.2		t	3	2.1	t
	1030	β-phellandrene								0.3	
	1031	1,8-cineole* [b]	t	t				t	45.5		t
	1050	(E)-β-ocimene							0.3	0.2	t
	1060	γ-terpinene						0.4	0.6	t	
	1070	*cis*-sabinene hydrate					0.6				
	1087	fenchone		1.6	3.9						
	1089	terpinolene						t			
	1097	linalool						0.5			
	1102	α-thujone [b]				82.3	85.7				
	1114	β-thujone				1.6					
	1141	verbenol		0.3							
	1142	*trans*-sabinol			0.2		0.2				
	1143	*cis*-sabinol		0.2							

Table II. Percentage composition of the essential oils of *Lantana canescens* (Lc1,Lc2), *Lantana tilcarensis* (Lti), *Lantana trifolia* (Ltr), *Aloysia citriodora* (Aci5, Aci6), *Aloysia gratissima* (Ag), *Aloysia castellanosii* (Acas) and *Aloysia catamarcensis* (Acat), CONTINUED

RI	RI										
Supelcowax 10	**DB-5**	**Compounds[a,c]**	**Lc1**	**Lc2**	**Lti**	**Ltr**	**Aci5**	**Aci6**	**Ag**	**Acas**	**Acat**
	1165	pinocarvone					1.7	t			
	1169	borneol				0.3					
	1177	terpinen-4-ol	t	t		1.7	0.6	0.1	0.6		
	1189	α-terpineol						0.5			
	1229	*cis*-carveol								0.1	
	1237	pulegone [b]					t				
	1238	neral		1		6	2		1.8		
	1243	carvone						0.8		98.7	
	1253	piperitone	t	0.1							
	1267	geranial				3.8	12.1				
	1276	carvone oxide									t
	1283	*cis*-verbenyl acetate							1.3		
	1289	bornyl acetate							0.7		
	1290	thymol [b]							17.4	0.1	
	1299	carvacrol							0.1		
	1335	*cis*-piperityl acetate	t	t							
	1338	δ-elemene		2.1	1.4			2.3			
	1351	α-cubebene				3.2			1.7	0.2	
	1352	thymyl acetate								0.2	0.1
	1373	carvacryl acetate							8.2		
	1375	α-ylangene		0.1							
	1377	α- copaene							0.1		
	1381	geranyl acetate				10.5				0.1	
1503	1388	β-bourbonene *			1	1.9					
1539	1388	β-cubebene *								0.1	
	1391	β-elemene	3.3	2.2	3.9	18.5					
	1408	longifolene			0.9				0.7		
	1419	β-caryophyllene			1.1	4.2	1.5			8.7	
	1434	β-gurjunene			2.3						
	1437	γ-elemene	0.3	0.5	1.9					0.4	
	1439	β-humulene				1.8					
	1441	aroma-dendrene	3.1	0.8							
	1443	(Z)-β-farnesene	13.9	8.8	4.4						
	1455	α-humulene	3	2.8	0.1	15.2			2.1	1.7	0.1
	1457	(E)-β-farnesene			27.5						
	1483	germacrene D	0.2	0.5	26.8	0.3	0.1		0.2		
	1498	α-selinene			0.8						
1719	1500	α-muurolene *	1	0.8					3.1		
1751	1500	bicyclogermacrene *	1	0.8		0.7	0.3				
	1506	β-bisabolene	9.3	4.4							
	1507	(Z)-α-bisabolene			3.5						
	1514	γ-cadinene	1	1.2	2.1	21.7				0.4	
	1523	δ-cadinene	2.1	1.1					0.5		
	1539	α-cadinene	1.1	0.9	9.6					0.8	
	1540	*cis*-calamenene							1.1		
	1546	α-calacorene							0.2		
	1561	germacrene B			0.6			t	0.5	0.4	
	1576	germacrene D-4-ol			1.3						
	1578	spathulenol	14.6	29.5					8.7	12.8	0.2
	1583	caryophyllene oxide	9.8	3.7						1.1	
	1585	globulol	0.2	0.5							
	1608	humulene epoxide II				1.5					
	1640	epi-α-cadinol (= tau-cadinol)		2.2	4.2		1.7				
	1646	α-muurolol	25.1	30							
	1654	α cadinol		0.5							
	Identified components		91.8	93.1	92.3	90.1	99	99.9	98.1	96.6	99.3
	Monoterpene hydrocarbons		0.6	0.3	0.2	0.2			19.6	49.6	
	Oxygenated monoterpenes			0.1	3.3	16.1	97.1	99.9	58.1	19.6	99
	Sesquiterpene hydrocarbons		39.3	24.8	87	70.6	1.9		11.7	13.5	0.1
	Oxygenated sesquiterpenes		51.9	67.9	1.8	3.2			8.7	13.9	0.2

a) Retention index, b) peak enrichment, c) mass spectra, e) compounds listed in order of elution from a DB-5 column. *) the compounds identified by Supelcowax 10.

these genera are closely related (3,9,10,11).

From the chemical point of view, the essential oils of some *Aloysia* and *Lantana* have been previously investigated (3). Thus, mono- and sesquiterpenes have been identified in the oils of *A. citriodora* (11,12,13,14,15,16,17), *A.gratissima* (6,11,14) and *L. canescens* (syn. *Lippia alba*) (10). However, there are no reports on the oils of *A. castellanosii, A. catamarcensis, L. trifolia* and *L. tilcarensis*. In the present study, the oils from seven species of Verbenaceae with several traditional uses in Argentina were analyzed.

Experimental

Plant material: A list of the plants studied, including the botanical name, voucher specimen and data related to traditional use are listed in Table I. Voucher specimens of each species were deposited at Jujuy Herbarium (JUA), University of La Rioja Herbarium (IZAC) and INTA EEA La Rioja Herbarium (CHAM).

Essential oil isolation: Dried leaves (100 g) of aromatic plants were hydrodistilled for 2 h using a Clevenger-like apparatus. The oils obtained were dried over anhydrous sulphate and stored in a refrigerator until analysis.

Gas chromatography analyses: Analyses were performed in a Shimadzu GC-R1A (FID) gas-chromatograph, fitted with a 30 m x 0.25 mm (0.25 µm film thickness) fused silica capillary column coated with a phase 5% phenyl 95% dimethylpolysiloxane, non-polar DB-5 column, followed by use of a polar Supelcowax 10 capillary column, phase polyethyleneglycol. The GC operating conditions were as follows: oven temperature programmed from 40–230^{0}C at 2^{0}C/min, injector and detector temperatures 240^{0}C. The carrier gas was nitrogen at a constant flow of 0.9 mL/min. The constituents of the oils were identified on the basis of their GC retention indices (RI) with reference to a homologous series of n-alkanes (C_{12} - C_{25}), by comparison of their retention times with those of pure authentic samples from Sigma, Fluka and Palma Companies, peak enrichment on co-injection with authentic standards wherever possible, by GC/MS library search (Adams and NIST) and using visual inspection of the mass spectra from literature, for confirmation. GC/MS analyses were performed with a Perkin Elmer Q-700 equipped with a SE-30 capillary column (30 m x 0.25 mm; coating thickness 0.25 µm film). The analytical conditions were: oven temperature from 40–230^{0}C at 2^{0}C/min, the carrier gas was helium at a constant flow of 0.9 mL/min, the source was at 70 eV. Scan 1,4/ seg. Scan parameters: Low mass 33 UMA; high mass 550 UMA.

Results and Discussion

As shown in Table II, 25 compounds of the essential oils of *L. canescens* were identified representing > 91.8%. The main compounds with concentration higher than 8.0% were the sesquiterpenes: β-bisabolene (4.4–9.3%), caryophyllene oxide (3.7–9.8%), (Z)-β-farnesene (8.8–13.9%), spathulenol (29.5–14.6%) and α-muurolol (30.0–25.1%). These percentage variations found between the population of *L. canescens* for Calilegua National Park and Chijra place could be associated with the geographical origin of the material. The oils from *L. tilcarensis* and *L. trifolia* were rich in sesquiterpene hydrocarbons (> 70%). Thus the main components of *L. tilcarensis* were (E)-β-farnesene (27.5%), germacrene D (26.8%) and α–cadinene (9.6%), while the oil of *L. trifolia* was rich in β-elemene (18.5%), α-humulene (15.2%) and γ-cadinene (21.7%).

On the other hand, certain studies have mentioned that *A. citriodora* displays chemical variation. Thus, three chemotypes were reported: chemotype 1 characterized by the occurrence of 1,8-cineole and a higher percentage of α–pinene and α-curcumene (17); chemotype 2 characterized by a higher percentage of sabinene, α–thujone and citronellal (12,14); and chemotype 3 characterized by the most representative chemical profile of *A. citriodora*, higher percentages of neral, geranial and limonene (11,12,15,16). The results of the present study show that the two populations of *A. citriodora* had unusually high contents of α–thujone as the chemotype 2 mentioned by Gil et al. (12), but sabinene and citronellal were not detected.

These authors' present findings demonstrate that the chemical composition of the oil of *A. gratissima* also varies considerably depending upon the plant origin. Thus, results showed that the main components were 1,8-cineole (45.5%), sabinene (8.3%), carvacryl acetate (8.2%) and spathulenol (8.7%) from northwest Argentina. These results show remarkable differences with previously reported studies for this species. Ricciardi et al. (18) showed as principal constituents β-elemene (35.7%); viridiflorol (33.6%); β-caryophyllene (28%); α-thujone (17.5%); 10-epi-cubebol (13.4%); bicyclogermacrene (12.8%); (E)-nerolidol (11.6%); and germacrene D (10.1%) from samples obtained from eastern Argentina, and Zygadlo et al. (14) showed as principal constituent pulegone (65.8%) from samples of flowers of plants grown in central Argentina. While Duschatzky et al. (19) and Bailac et al. (20) reported that α-cadinol (17.4% and 33%, respectively) was the main component from oil samples obtained from plants collected in west central Argentina. Thus, further studies on *A. gratissima* should be cognizant of the occurrence of chemotypes in natural plant populations and the impact that this would have on their use as medicinal herbs. Because these plants are used by many ethnic groups for treatment of various ailments, differences in the content and composition of the oils could be show differential effects on their efficacy.

A. catellanosii was characterized by high content of sabinene (44.8%), thymol (17.8%) and spathulenol (12.8%), while *A. catamarcensis* was characterized by high content of carvone (98.7%).

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