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**Northwestern Argentina: a Center of Genetic Diversity of Lemon Verbena
(*Aloysia citriodora* Palau, Verbenaceae)**by Paola Di Leo Lira^a), Catalina M. van Baren^a), Simon López^b), Ana Molina^c), Cecilia Heit^c),
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The aerial parts of lemon verbena (*Aloysia citriodora* Palau) are worldwide used due to their medicinal and aromatic properties. The essential-oil and acteoside contents have been proposed as the main quality markers for their pharmacological and organoleptic features. The northwestern region of Argentina has been repeatedly proposed as the place of origin for this species. For this reason, the essential-oil yields and chemical compositions of leaves of 25 populations of lemon verbena from both wild collections and experimental crops from this region were studied. Plants from six different collections were subsequently grown on the same experimental parcel located at Cerrillos, Salta province, during more than seven years. In addition, the acteoside contents determined in all the samples collected in 2010 showed significant variations (from 0.5 to 4.0%). Large differences were observed in the essential-oil composition and yields, which ranged from 0.4 to 2.1% (v/w). Nevertheless, most of the samples complied with the European Pharmacopoeia specifications. A remarkable chemical diversity with at least four clearly defined chemotypes was detected in this region. Therefore, it would be urgent to encourage actions to protect these genotypes of lemon verbena in the northwestern Argentina.

Introduction. – Lemon verbena, *Aloysia citriodora* Palau (syn.: *A. citrodora* PALAU, *A. triphylla* (L'HER.) BRITTON, *Lippia citriodora* (LAM.) KUNTH, *L. triphylla* (L'HER.) KUNTZE), belongs to the Verbenaceae family. Though the Northwestern Argentina has been proposed as the place of origin of this species [1][2], currently this South American aromatic plant has a widespread market in the occidental world. Infusions of the aerial parts are used in traditional medicine as antispasmodic, diuretic, digestive, cardiogenic, and sedative agents [3–6]. It is also widely employed in liquors and non alcoholic beverages. The typical fresh, lemony, and herbaceous scent has been ascribed to its essential-oil content, but other compounds, such as flavonoids and phenol derivatives, may contribute to the whole flavor profile. The contents of essential oil and acteoside, a bitter phenylpropanoid glucoside, have been proposed by the European Pharmacopoeia [7] as the main quality markers for this species, and although volatile and non volatile fractions are responsible of its pharmacological and organoleptic properties [8–10], the chemical composition of the essential oil was not considered.

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The essential-oil composition of commercially available lemon verbena as well as from plants cultivated in different countries has been reported [11–22]. In Argentina, several multidisciplinary groups have been working in collaboration on this species during the past ten years [23–26], detecting a remarkable chemical complexity. Large qualitative and quantitative variations were detected in the composition of the essential oils of plants collected at different locations of the Northwestern Argentina in coincidence with the area regarded as the origin of this species. No data on acteoside contents were reported in the previous works on lemon verbena from Argentina.

Herein, we report the chemical composition of the essential oils and acteoside contents in leaves of 25 wild populations and experimental crops of lemon verbena from Northwestern Argentina (Salta and Jujuy provinces). Six of them have been subsequently grown on the same experimental parcel located at Cerrillos, Salta province, during more than seven years. The aim of this work was to evaluate the chemical diversity of lemon verbena in this geographical area, and, more importantly, to confirm it as a probable center of genetic diversity. In this way, both actions should be encouraged for the protection of this source of genetic diversity of this species.

Results and Discussion. – *Essential-Oil Analysis.* The yields and chemical composition of the essential oils obtained from 25 samples of leaves of lemon verbena from wild populations and crops, harvested in different places of the Northwestern Argentina (Salta and Jujuy provinces) were determined. Twelve samples (labeled as 14D–25D) were harvested during 2010 from experimental crops located in Cerrillos, province of Salta, Argentina. Six of these samples (those labeled from 14D–19D) were also collected and analyzed from earlier harvests (2003/2004) and labeled as 14C to k, ^{19C} respectively. In addition, the results of the analyses of 13 cultivated or wild populations (labeled IV–13V) collected at different places of Northwestern Argentina (Salta and Jujuy provinces) were included in this study.

The yields of essential oils varied from 0.4 to 2.1% (v/w) (Table 1). Relative percentage compositions of the main compounds of the essential oil samples analyzed are compiled in Table 2. Only compounds present in more than 5% of the total oil in at least one sample were considered.

Significant qualitative and quantitative differences in the essential-oil composition were detected. In six cases (the pairs of samples labeled 14C and 14D–19C and 19D, resp.), the quality remained stable through the last seven years. To establish some correlation among these data, a cluster analysis (CA) was applied, showing a close match among some materials, but a very different cluster for others (Fig. 1). The highest similarities, over 99%, were found in 5V and 15C; 15D, 23D, and 20D; 18A, 18D, and 24D; 17C and 17D; 12V and 9V; 19C and 19D; 7V and 8V; 3V and 10V, 14C, 25D, 14D, and 16C; and 16D and 21D. Samples of equal numbers and different letters (C and D) corresponded to collections of the same place but harvested in 2003/2004 and 2010, respectively. The stability of the chemical profile during seven years in plants grown on the same parcel suggests the presence of true chemotypes, presumably four new types. With more than 75% of similarity, the analyzed samples were grouped into these four clusters:

Group I: 1V, 6V, 13V, 5V, 15C, 4V, 15D, 23D, 20D (limonene type)

Group II: 11V, 18C, 18D, 24D, 17C, 17D (carvone type)

Table 1. Source, Date of Harvest, and Essential-Oil Yields from Leaves Samples of the Collections of Lemon Verbena Analyzed

Sample	Date of harvest	Source		Crops	Yield [%]
		Locality	Zone ^{a)}		
1V	February 2003	San Salvador de Jujuy	Alto Comedero (JU)	yes	0.7
2V	February 2003	San Salvador de Jujuy	Alto Comedero (JU)	yes	0.8
3V	February 2003	San Salvador de Jujuy	Los Perales (JU)	yes	2.1
4V	February 2003	San Salvador de Jujuy	San Pedrito (JU)	yes	0.7
5V	March 2003	Salta	(SA)	yes	1.2
6V	February 2003	El Carmen	Severino (JU)	no	1.0
7V	February 2003	Tilcara	Tilcara (JU)	no	0.7
8V	May 2003	Humahuaca	Chucalezna (JU)	no	1.1
9V	May 2003	Humahuaca	Chucalezna (JU)	no	0.4
10V	March 2003	San Antonio	Los Alisos (JU)	yes	0.7
11V	February 2003	Tilcara	Juella (JU)	no	0.5
12V	February 2003	Guerrero	Guerrero (JU)	no	1.9
13V	March 2003	El Carmen	El Carmen (JU)	yes	1.0
14C	March 2003	Chicoana Quebrada de Escoipe	San Martín (SA)	yes	0.9
14D	January 2010	Chicoana Quebrada de Escoipe	San Martín (SA)	yes	1.1
15C	March 2003	Chicoana Quebrada de Escoipe	Quebrada el Sunchal (SA)	yes	0.8
15D	January 2010	Chicoana Quebrada de Escoipe	Quebrada el Sunchal (SA)	yes	0.9
16C	March 2003	Chicoana Quebrada de Escoipe	San Martín (SA)	yes	0.6
16D	January 2010	Chicoana Quebrada de Escoipe	San Martín (SA)	yes	0.7
17C	March 2003	Chicoana Quebrada de Escoipe	Quebrada La Apacheta (SA)	yes	0.5
17D	January 2010	Chicoana Quebrada de Escoipe	Quebrada La Apacheta (SA)	yes	1.0
18C	March 2003	Chicoana Quebrada de Escoipe	Quebrada La Apacheta (SA)	yes	0.5
18D	January 2010	Chicoana Quebrada de Escoipe	Quebrada La Apacheta (SA)	yes	0.8
19C	March 2004	Chicoana Quebrada de Escoipe	Quebrada el Sunchal (SA)	yes	0.4
19D	January 2010	Chicoana Quebrada de Escoipe	Quebrada el Sunchal (SA)	yes	0.6
20D	January 2010	Chicoana Quebrada de Escoipe	Quebrada el Sunchal (SA)	yes	0.9
21D	January 2010	Chicoana Quebrada de Escoipe	Quebrada La Apacheta (SA)	yes	0.7
22D	January 2010	Chicoana Quebrada de Escoipe	Quebrada el Sunchal (SA)	yes	0.9
23D	January 2010	Chicoana Quebrada de Escoipe	Quebrada el Sunchal (SA)	yes	0.9
24D	January 2010	Chicoana Quebrada de Escoipe	San Martín (SA)	no	1.0
25D	January 2010	San Carlos	La Punilla (SA)	no	0.5

^{a)} JU: Jujuy province; SA: Salta province

Group III: 9V, 12V, 19C, 19D, 22D (thujones, sabinone type)

Group IV: 2V, 7V, 8V, 3V, 10V, 14C, 25D, 14D, 16C, 16D, 21D (citronellal-citral type)

In contrast to what was observed in other areas of our country or elsewhere, excellent qualitative and quantitative differences were found in the volatile profile of lemon verbena samples collected in Northwestern Argentina. As it is shown in Table 2, the essential oils from samples 9V, 12V, 19C, 19D, and 22D were characterized by the presence of thujones ($\alpha + \beta$, 61.4–80.5%), sabinene (2.2–9.3%), and sabinone (2.4–5.6%) as main compounds. Sabinone could not be identified by traditional analytical methodologies, since neither its mass spectrum nor its retention index (RI) on GC were available from commercial libraries [27][28]. Though the mass spectrum of sabinone

Table 2 (cont.)

Sample	15C	15D	16C	16D	17C	17D	18C	18D	19C	19D	20D	21D	22D	23D	24D	25D
Sabinene	0.8	0.3	18.3	26.6	0.6	0.3	0.3	0.3	9.3	6.1	0.3	28.0	5.8	0.3	0.8	13.1
Santolina alcohol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Limonene	37.7	55.2	0.1	1.1	25.9	29.8	42.2	52.5	0.3	0.3	47.1	0.2	0.2	58.5	42.6	0.2
1,8-Cineol	-	1	1.0	-	-	0.4	0.2	0.9	0.7	0.4	0.5	2.1	0.6	0.4	0.3	0.3
α -Thujone	-	0.1	1.4	2.3	6.0	5.9	1.6	1.7	46.8	59.0	0.4	2.8	79	0.1	3.0	1.2
β -Thujone	-	0.3	-	-	0.1	0.1	0.2	-	26.6	20.4	0.4	0.6	1.5	-	-	-
(<i>E</i>)-Limonene oxide	2.5	0.9	-	-	6.6	3.3	0.4	-	-	-	0.9	-	-	1.0	0.3	-
Citronellal	23.3	9.5	70.7	41.9	1.8	0.4	-	-	-	0.1	10.3	37.1	0.3	7.6	0.9	58.7
Sabinone	-	-	-	0.1	-	-	-	-	5.2	5.6	-	0.1	4.4	-	-	-
(<i>Z</i>)-Dihydrocarvone	-	0.6	-	0.1	11.6	10.6	-	0.6	-	0.1	-	-	-	0.7	5.2	0.1
(<i>E</i>)-Dihydrocarvone	-	0.2	-	-	35.2	31.8	-	0.2	-	-	-	-	-	0.1	0.5	-
Neral	9.6	5.5	1.2	2.1	-	-	-	-	-	-	7.3	0.2	-	4.6	-	0.6
Carvone	-	1.6	-	0.2	1.1	2.0	37.0	30.7	-	0.2	1.8	0.3	0.1	2.2	24.3	1.4
Geranial	10.2	6.7	0.1	2.8	-	-	-	-	-	-	8.9	0.2	-	5.6	-	0.8
Thymol	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Piperitenone	-	-	-	-	-	-	-	-	-	-	-	-	-	-	4.6	-
<i>ar</i> -Curcumene	0.6	0.9	-	1.5	0.1	0.9	-	-	0.1	0.7	1.3	0.1	0.5	0.8	1.1	1.2
Spathulenol	0.5	1.1	0.7	2.1	0.2	0.9	-	-	0.3	0.2	1.1	1.1	0.4	1.2	0.7	1.6
Caryophyllene oxide	0.7	1.4	-	-	0.4	0.5	0.6	0.9	-	0.1	1.7	0.3	0.2	1.5	0.2	3.3
Acteoside	-	2.9	-	4.0	-	1.8	-	3.6	-	2.4	3.0	2.2	2.5	3.6	0.5	0.6

^{a)} -; Not detected or less than 0.1%.

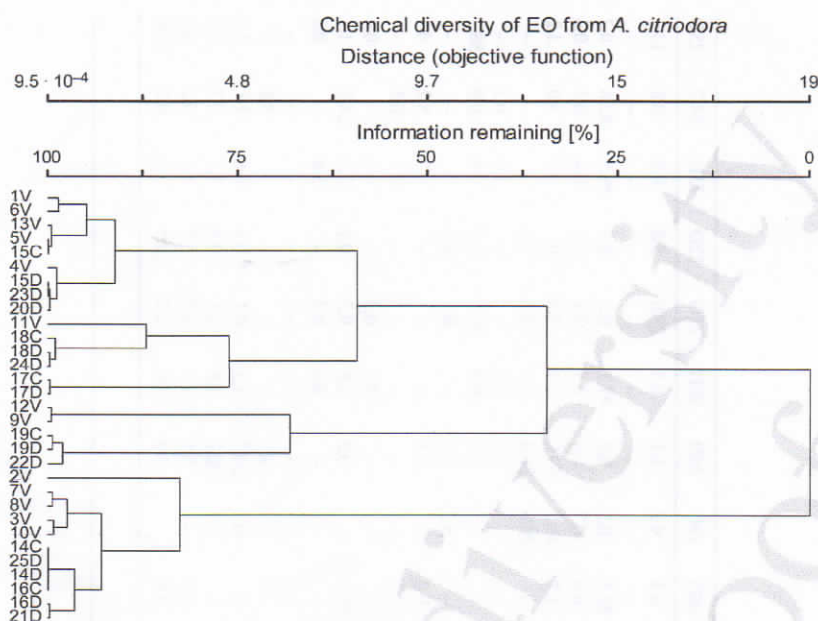


Fig. 1. Dendrogram showing the chemical diversity of essential oils of *Aloysia citriodora* analyzed

(see Fig. 2) shows some similarities with those of umbellulone and pinocarvone [27][28], the retention indexes (*RI* 1154 in a nonpolar column; 1594 in a polar column) were significantly lower than those reported for umbellulone (*RI* (non polar), 1167; *IR* (polar), 1644) and pinocarvone (*RI* (non polar), 1160; *IR* (polar), 1561). Besides, the UV spectrum, in EtOH ~~and at 96%~~, of essential-oil samples 19C, 19D, and 22D, containing sabinone, displayed an absorption maximum at 258 nm which is not coincident with the absorption maximum of umbellulone (λ_{\max} 265 nm) or pinocarvone (λ_{\max} 242 nm) [29]. The mass spectrum of our ketone was shown to be identical with that of synthetic sabinone obtained by pyridinium chlorochromate (PCC) oxidation of sabinol (spectrum provided by Dr. *Patrick Covello*, Plant Biotechnology Institute, National Research Council, Canada). Final confirmation of the identity of sabinone was provided by $^1\text{H-NMR}$ spectrum (200 MHz, CDCl_3) of a sample isolated by column chromatography from essential oil 19D: 5.74 and 5.25 (2s, $\text{H}_a\text{-C}(10)$ and $\text{H}_b\text{-C}(10)$), 2.47 (dd, $J = 19, 2.7$, $\text{H}_\alpha\text{-C}(2)$), 2.28 (d, $J = 19$, $\text{H}_\beta\text{-C}(2)$), 2.01 (dd, $J = 3.5, 8.1$, $\text{H-C}(5)$), 1.46 (sept., $J = 6.7$, $\text{H-C}(7)$), 1.04 (ddd, $J = 8.1, 5.3, 2.7$, *exo*- $\text{H-C}(6)$), 0.95 and 0.90 (2d, $J = 6.7$, $\text{Me-C}(8)$ and $\text{Me-C}(9)$), 0.40 (dd, $J = 5.3, 3.5$, *endo*- $\text{H-C}(6)$), identical to those reported for synthetic sabinone [30].

To the best of our knowledge, this is the first time that sabinone is reported in an essential oil.

In addition to α -thujone, β -thujone, and sabinone, all of the five essential oils from Group III (samples 9V, 12V, 19C, 19D, and 22D) contained sabinene and minor

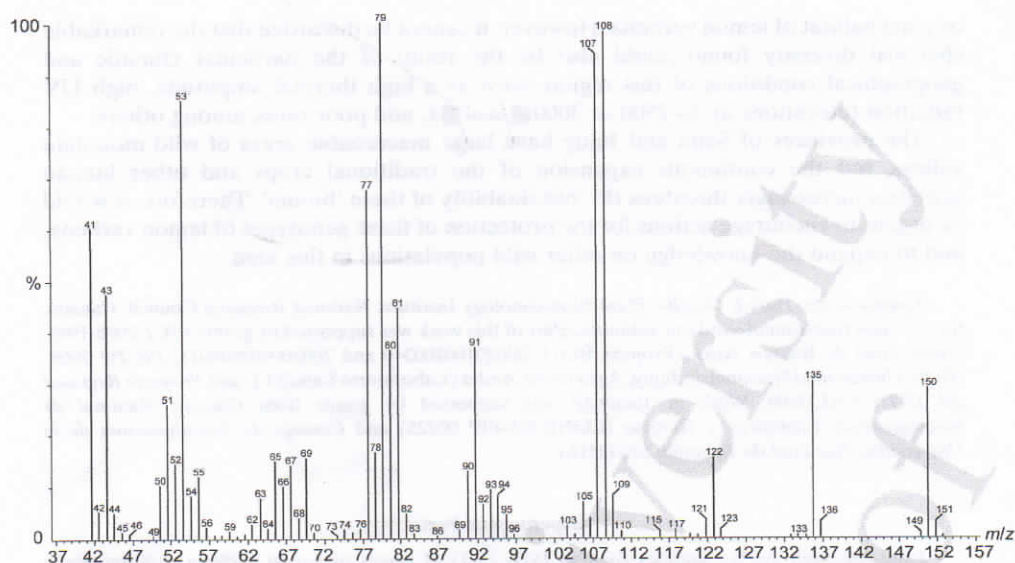


Fig. 2. Mass spectrum of sabinone

amounts of sabinol (*Supplementary Material*, not included in *Table 2*). The co-occurrence of these five thujane derivatives in *Aloysia citriodora* strongly suggests that the thujones are biosynthesized following a pathway similar to the biogenesis of thujones in sage (*Salvia officinalis*), common tansy (*Tanacetum vulgare*), and wormwood (*Artemisia absinthium*), i.e., sabinene → sabinol → sabinone → thujone, as previously proposed by *Croteau* and co-workers [31–33].

Acteoside Contents. Samples from experimental crops harvested in 2010, *14D–25D*, were also analyzed for acteoside contents in order to estimate the quality of plant material according to the European standards [7], which require a minimum of 0.2% of essential-oil yield for dried leaves and a minimum of 2.5% of acteoside. In addition, some proposals for standards of lemon verbena based on the chemical composition of the essential oil have been reported [18][26]. It is remarkable that none of the samples studied in this work complied with these latter specifications, but six of them, *15D, 16D, 18D, 20D, 22D* and *23D*, did conform to the European standards [7], in spite of their atypical volatile profiles with low or null contents of citral. For this reason, it would be comprehensible to extend the specifications of the European standards including specifications for the aromatic profile. This could at least improve the quality of lemon verbena in our country.

Conclusions. – Even if there is not a taxative connection between a center of genetic diversity and the original habitat of the species, a strong relationship between them is expected. Our results are in agreement with the suggestions of other authors who, using different ways [1][2], concluded that the Northwestern Argentina is probably the

original habitat of lemon verbena. However, it cannot be discarded that the remarkable chemical diversity found could also be the result of the particular climatic and geographical conditions of this region, such as a high thermal amplitude, high UV radiation (elevations up to 2500 or 3000 msl), and poor rains, among others.

The provinces of Salta and Jujuy have large inaccessible areas of wild mountain valleys, but the continuous expansion of the traditional crops and other human activities increasingly threatens the sustainability of these 'bioma'. Therefore, it would be urgent to encourage actions for the protection of these genotypes of lemon verbena, and to expand the knowledge on other wild populations in this area.

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Experimental Part

Plant Material. Twelve samples (named 14D–25D) of leaves of lemon verbena experimentally cultivated at Estación Experimental Agropecuaria de INTA-Cerrillos (province of Salta, Argentina) were collected. Also, unpublished data from earlier harvests of six of these materials, 14C–19C, and from 13 cultivated or wild populations, 1V–13V, from different places of Northwestern Argentina (Salta (SA) and Jujuy (JU) provinces) are presented. Data for each sample are compiled in *Table 1*. Geographical locations of the sampled populations are indicated in *Fig. 3*. All the plant material was identified by one of the authors (S. L.) or by Dr. *Gustavo Giberti* (Facultad de Farmacia y Bioquímica, University of Buenos Aires).

Essential-Oil Extraction. The essential oils of samples D and C were obtained from air-dried parts of the plant materials by hydrodistillation for 2 h with a *Clevenger*-type apparatus [7]. Samples labeled V were extracted by steam distillation with a *Clevenger* trap. The collected oil samples were dried (Na_2SO_4) and stored at 4° until analysis by GC/MS.

Analysis of the Essential Oils of Samples D. A GC-FID/MS system, *Perkin-Elmer Clarus 500* was used with an autosampler and a unique injector (split ratio: 1:100) connected by a flow splitter to two columns: a) polyethyleneglycol PM ca. 20,000, and b) 5% phenyl/95% methyl silicone, both 60 m × 0.25 mm with 0.25-μm film thickness. The polar column was connected to a flame ionization detector (FID), while the nonpolar column was connected to a FID and a quadrupolar mass detector (70 eV) with a vent system (*MSVent*TM). Carrier, He; flow rate, 1.87 ml/min. The oven-temp. program: 90° to 225° at 3°/min, and then isothermic for 15 min. Injector and both FID temps. were set at 255° and 275°, resp. Injection: 0.2 μl of a 10% soln. of oil in EtOH. The temp. of the transference line and the ion source were 180° and 150° resp.; the range of masses was 40–300 Da.

Analysis of the Essential Oils of Samples C. A GC/MS *HP 6890* connected to a mass spectra detector *HP 5973* was used. Column: *Elite 5 MS* (*Perkin-Elmer*; 30 m × 0.25 mm with 0.25-μm film thickness). Carrier, He; flow rate, 1 ml/min. The temp. program: 60° (1 min); 60–185° (1.5°/min); 185° (1 min); 185–275° (9°/min); 275° (2 min). Injector temp.: 250°. Injection: 0.2 μl (split: 1:80). Temp. of the transference line: 280°; quadrupole: 150°; ion source: 230°. For quant. determinations, a *Hewlett Packard 5890 Series II* gas chromatograph equipped with a FID and a cap. *HP-5* column (30 m × 0.32 mm with 0.25-μm film thickness) was used. Carrier gas, N_2 ; flow rate, 1.2 ml/min. Detector temp.: 280°; injector temp.: 250°. Injection: 0.2 μl (split 1:70). The oven temp. program was the same as above.

Analysis of the Essential Oils of Samples V. A GC-FID *KONIK KNK 3000G* equipped with a split injector was used. Column: *HP-5* fused silica cap. column (30 m × 0.25 mm with 0.25-μm film thickness).

MSL

0.25-μm

gas

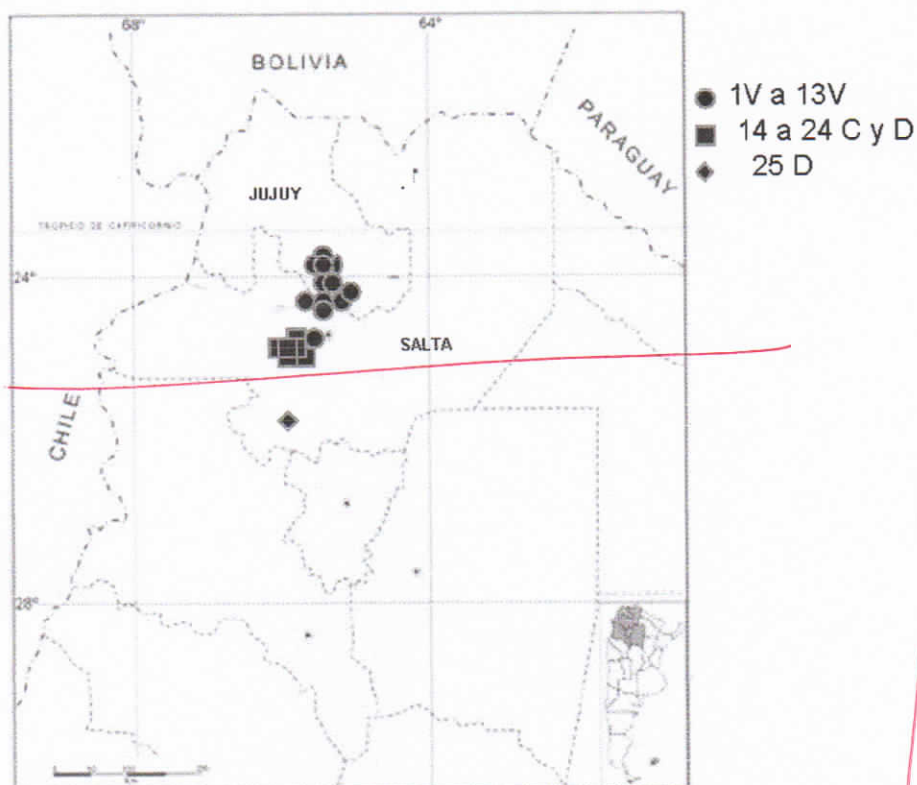


Fig. 3. Geographical location of the sampled populations

Carrier gas, H_2 ; flow rate, 1.2 ml/min. The oven-temp. program: 60° (5 min), 60° – 230° (6° /min). FID temp.: 300° ; injector temp.: 250° . GC/MS Analysis was carried out on a Hewlett Packard GC 6890/5972. Column: HP-5 MS (30 m \times 0.25 mm; 0.25- μ m film thickness) and a H_2 carrier gas flow of 0.7 ml/min. The oven temp. program was the same as above; the temp. of the transfer line (300°) and of the injector (250°) were held constant during analyses.

Compound Identification. The identification of the compounds in the essential-oil samples was based on *i*) computer matching with commercial mass-spectra libraries [7][8]; *ii*) laboratory-developed mass-spectra libraries built up from components of known oils and authentic samples; and *iii*) by comparison of the retention indices (RIs; relative to C_8 – C_{25} alkanes) obtained using one column (samples C and V) or two different columns (samples D) with those of reference compounds. The relative percentage composition was determined using the single area percentage method, without considering corrections for response factors. When two columns were simultaneously used, the lowest response obtained from each column for each component was considered. Only volatile compounds which were present over 5% of the total oil in at least one of the samples were considered. Percentages of compounds below 0.1% or not detected are shown as ‘-’.

Determination of Acteoside Contents. The plant material was analyzed according to *European Pharmacopoeia 7.0*. An 60% (v/v) EtOH extract for each sample was evaluated using a HPLC system consisting of a Perkin–Elmer 200 instrument with a diode array detector. Sample injection was performed with a Perkin–Elmer series 200 auto-injector fitted with a 20 μ l sample loop. The column was a

Lichrosorb RP18 (250 mm × 4 mm i.d., 5 μ) with a pre-column of the same phase. The mobile phase was 0.3% (v/v) soln. of H₃PO₄ (A) and MeCN (B). The following multi-step linear gradient was achieved using a *Perkin–Elmer* series 200 pump set at 1 ml/min: 0–20 min, 93–83% A; 20–30 min 83% A; 30–35 min, 83–75% A; 35–40 min, 75–20% A; 40–45 min 20–93% A. The UV/VIS spectra were recorded between 220–500 nm, and the chromatographic profiles were registered at 330 nm.

Data Analysis. The PC-ORD software [34] was used to generate a distance matrix and a dendrogram based on the essential-oil composition data. The cross products matrix was obtained by the correlation, and cluster analysis was conducted by the relative Euclidean and *Ward's* linkage methods.

Supporting Information Available. The full chemical compositions of all the essential-oil samples analyzed are available upon request from the corresponding author.

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