Essential Oils from Argentinean Aromatic Plants

Hector R. Juliani, Adolfina Koroch and James E. Simon
New Use Agriculture and Natural Plant Products Program
Rutgers University, New Brunswick, New Jersey, U.S.A.

Fernando N. Biurrun
Instituto de Desarrollo de los Llanos de La Rioja
National University of La Rioja
La Rioja, Argentina

Veronica Castellano, and Julio A. Zygadlo
Instituto Multidisciplinario de Biologia Vegetal (IMBIV-CONICET) –
National University of Córdoba, Argentina

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Abstract

A research association was established between Rutgers University, USA and Argentinian Universities, National University of La Rioja and National University of Córdoba, to identify aromatic and medicinal plants of potential commercial interest for future cultivation and conservation programs. This study was part of a larger project to study the uses of native aromatic plants in commercial products in Argentina and to evaluate the content and composition of essential oils in some of the species growing wild in the Los Llanos region (La Rioja Province, midwestern Argentina).

A regional market survey showed that the majority of these species are utilized commercially to prepare a wide range of commercial herbal products that include non-prescription drugs, composite yerba mate, herbal teas and non-alcoholic beverages. *Lippia turbinata*, locally known, as "Poleo" was the most used aromatic plant in Argentina, being found in the 38 % of commercial products, whereas, *L. integrifolia* ("incayuyo") was present in 23 % of products. *Chenopodium ambrosioides* ("paico") and *Aloysia polystachia* ("Te del burro") were found in 5 % and *A. gratissima* ("Palo amarillo") in only 1 % of commercial herbal products. The essential oil of these species and other aromatic plants from Los Llanos region (La Rioja Province) were evaluated. We found that several of the aromatic plants from this region of Argentina could serve as potential new sources of essential oils. In addition, the volatile oils of *Lippia salsa* and *Larrea divaricata* are described for the first time.

INTRODUCTION

In Argentina, local people commonly use aromatic plants in popular medicines and as beverages (Soraru and Bandoni, 1978). As a consequence, this important group of the native flora is found in a wide variety of commercial products (Zygadlo and Juliani, 2002). In recent years, there appears to be a significant increase in their consumption and demand. Since very few of the native species are cultivated, nearly all are collected from the wild to meet the growing demands of industry. As a result, natural populations are declining and genetic diversity has been lost, and the scientific and environmental communities are concerned that further genetic losses will be witnessed in the future without purposeful intervention (Oni, 1993). Prior work showed that many of the therapeutic effects of these species in their local applications could be attributed predominantly or even exclusively to their essential oils (Trease and Evans, 1986).

Essential oils extracted from plants have long been used in foods, flavorings and fragrances (Williams, 1997). Those plants, which provide new and unique fragrances and

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aromas, have potential for commercialization as new crops either as culinary herbs, aromatic teas, or as sources of extractable essential oils (Simon, 1990). A research association was established between Rutgers University, USA and Argentinian Universities, National University of La Rioja and National University of Córdoba, to identify aromatic and medicinal plants of potential commercial interest for future cultivation and conservation programs. The aim of this work was to study the uses of native aromatic plants in selected commercial products in Argentina and to evaluate the content and composition of essential oils in some of this species growing in Los Llanos region (La Rioja Province, Midwestern Argentina).

MATERIAL AND METHODS

A regional market survey of local supermarkets was conducted. In total 82 commercial products were found being sold in supermarkets containing one or more native aromatic plants. The commercial products containing native herbs were clustered into four main groups of products (non-prescription drugs, composite yerba mate, herbal teas, and non-alcoholic beverages). The collection of products and relative popularity or use of the herb was expressed as a percentage that the given aromatic species was present in a given group of products or in the whole set (Table 1). The volatile essential oils from plants growing in the wild in the region of "Los Llanos" (La Rioja Province, Midwestern Argentina) were extracted by steam distillation. The volatile oil was analyzed by a gas chromatograph (GC) coupled to a mass spectrometer (MS) and Flame ionization detectors (FID) (Agilent GC System 6890 Series, Mass Selective Detector, Agilent 5973 Network, FID detector). Samples were injected with an autosampler (Agilent 7683 Series), the Inlet temperature was 220 °C., in a HP5- MS (30 m, 0.25 ID, 0.25 mm) column, temperature program, 60 °C 1 min, 4 °C/min, 200 °C 15 min. Helium constant flow was set at 1 ml/min. Individual identifications were made by matching their spectra with those from mass spectral libraries (Wiley 275.L). Components were listed in order of elution in HP5 (DB5 equivalent) column.

The native species included in this study were *Aloysia grattissima*, *Aloysia polystachia, Chenopodium ambrosioides, Lippia integrifolia, Lippia salsa, Lippia turbinata*, *Larrea divaricata*. Voucher specimens were deposited at the "Herbario Regional de Chamical" (IZAC) National University of La Rioja.

RESULTS AND DISCUSSION

Commercial Uses of Aromatic Plants in Argentina

The market survey showed that the majority of these species are utilized commercially to prepare a wide range of commercial product that include non-prescription drugs, composite yerba mate, herbal teas and non-alcoholic beverages (Table 1). Non-prescription drugs are made by packages containing 10-50 g of dried plant parts (usually the leaves of single species) that are used in popular medicine, mainly as digestive, diuretic anti-inflammatory, laxative, among others. In general, they are predominately composed of *Lippia turbinata*, locally known as "Poleo" and *Lippia integrifolia* known as "incayuyo" (Table 1).

The composite yerba mate is a mixture of *Ilex paraguariensis* leaves (generally consisting of 85-95 % of the total product) that is utilized for the preparation of the traditional beverage "mate." These products were often blended with of native aromatic plants for flavor (from 5-15 % of total product weight), of which *L. turbinata* was also found in almost 90 % in this group of products (Table 1).

Herbal teas are made in tea bags containing 1.5-3 g of dry aromatic plants that are used not only for medicinal purposes (mainly digestive) but also for flavoring. They were found to be composed of a single native species or as a mix of several native and/or foreign aromatic plants including but not limited to *Mentha sp* (Mint), *Matricaria recutita* (Chamomile), *Cinnamomum zeylanicum* (Cinnamon) and *Pimpinella anisum* (Anise). In herbal teas, the native plants were a minority group, *L. turbinata* and *L. integrifolia* and

were found in only ca. 25 % of the products while the majority of teas were dominated by mint (60 %) and chamomile (53 %) (Table 1). Noteworthy is that the most important aromatic crops in Argentina are mint and chamomile (Vallejos, 2000).

Finally, the non-alcoholic beverages group included bitter beverages called "amargos" that are prepared mainly with species of the genus *Baccharis* and are flavored with native aromatic plants. The "amargos" are sold in one-liter bottles and are of high demand because of use in treating digestive problems. In this product group, *L. turbinata* and *L. integrifolia* (locally known as "Incayuyo") were found in 70 and 80 % of the products (Table 1).

Considering the total number of analyzed products (in total 82 items), *L. turbinata* was the most used aromatic plant in this region of Argentina, being found in the 38 % of the products while *L. integrifolia* was found in the 23 %, *C. ambrosioides* and *A. polystachia* in the 5 % and *A. gratissima* only in 1 % of commercial items (Table 1).

Essential Oils of Native Aromatic Plants From "Los Llanos" Region (La Rioja)

The essential oil content of *A. gratissima* (*Verbenaceae*) from La Rioja Province was 0.5 % and was composed by γ-elemene (20 %), spathulenol (13 %) and globulol (19 %) (Table 2). In the Province of Cordoba, one chemotype was found to contain pulegone (66 %) (Zygadlo et al., 1994), while in San Luis Province another chemotype was reported that was rich in caryophyllene oxide (11 %) and cadinol (33 %) (Bailac et al., 1999). Our results showed that *A. gratissima* from La Rioja may constitute a new chemotype.

A. Polystachia accumulated high amounts of essential oils (3.4 %) and their main components were *cis* and *trans* thujone (90 %) (Table 2). These results agree with previous reports of a chemotype with high amounts of thujone (70 %) in the Province of Córdoba (Velazco-Nereguela et al., 1993). While in Tucuman Province, carvone, sabinene, β-pinene and limonene were reported as major components for this species (Huergo y Retamar, 1973). Chemotypes containing high levels of thujone maybe not suitable for consumption as medicinal plants, since this component was found to be a neurotoxic monoterpene (Tyler, 1996).

The essential oil content of *L. integrifolia* (*Verbenaceae*) was 1.2 % and showed high amounts of spathulenol (17 %), lippifoli-1(6)-en-5-one (22 %) and 4,5 seco-african-4,5-dione (23 %). In the Province of Tucuman, a chemotype was reported that also contained lippifoli-1(6)-en-5-one as a major component of the oil (Lampasona et al., 1999), whereas, in the flowers oils from Cordoba Province, the main constituents were reported to be limonene (13 %), camphor (19 %), and lippifoli-1(6)-en-5-one (19 %) (Zygadlo et al., 1995).

L. turbinata accumulated 1.1 % essential oil composed mainly of limonene (50 %) and piperitenone oxide (30 %) (Table 2). This is in agreement with Duschatzky et al (1998) who reported this species in another province, the San Luis Province, to contain an essential oil with similar amounts of limonene (43 %) and piperitenone oxide (25 %). In the Province of Cordoba, the essential oil of this species was also reported to be rich in limonene though not in piperitenone oxide (Fester et al., 1956). However, other studies have shown that the flowers and whole plant of this species can be dominated by thujone. (28-30 %) (Velasco-Negueruela et al., 1993). The chemotype from La Rioja Province is a more suitable chemotype for the consumption of medicinal plants, since these plants did not contain thujone.

The essential oil content in *L. salsa* was very low (less than 0.1 %), and only twenty percent of the oil was identified. More work on this identification of the volatile constituents is required. The identified constituents included ocimenone (7 %), β-cubebene (1.4 %), γ-gurjunene (1.6 %), and an unknown sesquiterpene as the major component. The genus *Lippia* is composed of aromatic shrubs that accumulate high amounts of essential oils (Velazco-Nereguela et al., 1993; Zygadlo et al., 1995; Juliani et al., 2002). Our current results showed that *L. salsa* is the only species of the genus that does not appear to accumulate volatile essential oils in significant amounts. This is also

the first report of the detection of volatile oils from *L. salsa*, a notable endemic aromatic plant from salt marshes of central Argentina.

The accumulation of essential oil in *Chenopodium ambrosioides* (Chenopodiaceae) was 1.7 % of which the oil was dominated by E-ocimenone (47 %) and 1,3,8 para-menthatriene (32 %) (Table 2). *C. amborosioides* locally known as "paico" usually contained high levels of ascaridol. Ascaridol has been reported as a genotoxic monoterpene (Gadano et al., 2002). Since the plants from La Rioja Province did not contain ascaridol, this chemotype may be more suitable for the consumption as medicinal plant.

In *Larrea divaricata*, only low yields of essential oil was detected (0.2 %), and in the essential oils extracted from the distillation water with hexane (and concentrated by rotary evaporation) we were able to detect α-thujene (2 %), limonene (2 %), ocimenone (3 %), tau-cadinol (8 %), and many unknown sesquiterpenes (molecular weight 204-222) (Table 2). This is also the first report of the detection of terpenes in this native Zygofilaceae from La Rioja Province.

The essential oil content of *P. ruderale* was 0.5 % and was characterized by high levels of sabinene (46 %) and spathulenol (25 %) (Table 2). It was reported in Bolivia, an oil with high levels of sabinene (64 %) (Loayza et al., 1999), whereas in Brazil the oil was dominated by limonene (75 %)(Bezerra et al., 2002; Andrade et al., 1994). Our results coincide with those from Bolivia and suggest the existence of two chemotypes, one dominated by sabinene and the other by limonene.

CONCLUSION

The present study showed that many native aromatic plants are used commercially in Argentina and some of them grew in the "Los llanos" regions of La Rioja Province. The essential oils of the aromatic plants showed a great variability in their essential oil content and composition. Our results showed that "Los Llanos" constitutes a new source of aromatic plants and essential oils with economic potential. The study of the active principles of the aromatic plants can contribute to value of the natural resources, for future cultivation, conservation and sustainability of this region of Argentina.

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Tables

Table 1. Commercial uses of aromatic plants in Argentina.

Plant	%TOTAL[1]	Non-prescription drugs[2]	Composite yerba mate[2]	Herbal teas[2]	Non-alcoholic beverages[2]
Number of products	**82**	**49**	**8**	**15**	**10**
Lippia turbinata	37.8	26.5	87.5	26.7	70.0
Lippia integrifolia	23.2	12.2	25.0	20.0	80.0
Mentha sp	24.4	8.2	87.5	60.0	0.0
Matricaria recutita	14.6	2.0	25.0	53.3	10.0
Ilex paraguariensis	9.8	0.0	100.0	0.0	0.0
Coriandrum sativum	4.9	0.0	12.5	6.7	20.0
Chenopodium ambrosioides	4.9	6.1	-	6.7	0.0
Aloysia polystachya	4.9	8.2	-	-	-
Anethum sp	2.4	0.0	-	13.3	0.0
Cinnamomum sp	1.2	0.0	-	-	10.0
Aloyisa gratissima	1	-	-	-	-

[1] The percentage that an aromatic species is present in the whole set.
[2] Or in a given group of products.

Table 2. Essential oil composition of selected Argentinian Aromatic plants.

Constituents	*Aloysia gratissima*	*Aloysia polystachia*	*Chenopodium ambrosioides*	*Larrea divaricata*	*Lippia salsa*	*Lippia turbinata*	*Lippia integri-folia*	*Porophyllum ruderale*
Yield of oil[1]	0.5	3.4	1.7	0.2	0.1	1.1	1.2	0.5
α-Thujene	0.3	0.6		2.1				
Sabinene		1.9						46.5
β- Pinene			10.3					
Myrcene	0.4	0.8		0.2			0.3	
γ-Terpinen-1-al	1.4							
α-Terpinene								0.8
p-Cymene					0.5	0.8		3.2
Limonene		1.9		2.3		48.1		
β-Ocimene								1.2
cis-Thujone		54.3						0.5
trans-Thujone		36						
1,3,8 p-Mentatriene			32.1					1.6
Cis- Pinene hydrate			11					
Trans-Pinocarveol	1.9							
Camphor							0.8	
cis-Pinocarveol	1.9							
α-Terpineol		0.2				1.1		
Z Ocimenone					7.4		3.7	
E-Ocimenone			46.6	2.8			0.3	
Carvone						0.9		
Piperitenone						1.1		
δ-Elemene	0.7							
Thymol acetate				0.3				
Piperitenone oxide						30.1		
Geranyl acetate	0.9							
β-Cubebene	2.3				1.4			
Unknown sesquiterpene (MW 204)					64.5			
Methyleugenol						1.8		
(E)-Caryophyllene	2.2	1.2				0.9		
γ-Elemene	19.7			0.1				
α-Humulene	1	0.2				0.1		
Alloaromadendrene	1.5							
γ-Gurjunene	7.7				1.6			
Biciclogermacrene	2.8							
Cubebol	5.6							

Constituents	*Aloysia gratissima*	*Aloysia polystachia*	*Chenopodium ambrosioides*	*Larrea divaricata*	*Lippia salsa*	*Lippia turbinata*	*Lippia integri-folia*	*Porophyllum ruderale*
Elemol	2.4							
Germacrene B	3.5							
Spathulenol	13.4			1.2		6.7	17.05	25.3
Lippifoli-1(6)-en-5-one							22.4	
Globulol	18.6							
Carotol	1.8							
β-Oplopenone				1.4				
α-Cadinol				7.6				
4,5 Seco-african-4,5-dione							23.4	
Total analyzed	90	97.1	100	19.8	77.5	91.61	68	79.1