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#### Chemical characterization of Citrus sp. Petitgrain from jujuy

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#### Introduction

The Rutaceae family is rich in species, thus comprising about 1600 to 2000 species in 150 genera and 7 subfamilies. These are mostly tree species which grow in tropical and subtropical regions. The genus *Citrus* (Rutaceae) is represented by small trees of Asian origin, naturalized after some time in the Mediterranean countries and more recently in America and Australia.

Citrus plants have different alternatives for their integral profitable use, such as products for food industry, perfumery and cosmetics, and even aromatherapic applications.

Argentina occupies the eighth place (2,000,000 tons/year) as world producer of Citrus fruits (FAOSTAT). Northeastern and northwestern Argentina (NEA and NOA, respectively) concentrate the citrus activity mainly in the production of fresh fruits, juices, essential oils (EO) by cold-press of fruits epicarps. The EO of fruits is the most widespread. From flowers and leaves are also obtained EO (neroli and petitgrain, respectively) of different chemical composition. The composition of petitgrain (pg) depends on the *Citrus* species, the cultivar plant region of

In the transition forest district of Jujuy *Citrus* fruits are grown for direct fruit consumption, essential oils, juices and concentrates production. The annual pruning of plants generates a waste of leaf material that would be profitable as a source of pg.

In this paper the constitution of volatiles from the residual leaf material of cultivars of *Citrus sinensis* (L.) Osbeck var. Hamlin (Hamlin orange), *C. reticulata* Blanco cv. Dancy (Dancy mandarin), *C. deliciose* Ten. (Creole mandarin) is evaluated (Citrus of the world, 2001).

#### Methodology

Tender leaves and stems (1 + s) of pruning material from three *Citrus* cultivars were selected, *e.g.*, Hamlin orange (*Citrus sinensis* (L.) Osbeck var. Hamlin), Dancy mandarin (*Citrus reticulata* Blanco *cv.* Dancy) and

Creole mandarin (Citrus deliciose Ten.) from the transition forest area, Jujuy, Argentina. The EO was extracted at a laboratory scale by cohobation-hydroextraction and at a pilot scale by a 100-litres steam self-generator. Volatile compounds were obtained by steam distillation and further separated from water, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and kept at 4°C until analysis. The EO were analysed by gas-liquid chromatography using a Hewlett Packard 6890 chromatograph with HP5 column (30 m), with a MSHP5972A mass detector and a flame ionization detector (FID). A series of *n*-alkanes was used as internal standards. The compounds were identified by MS analysis, and retention times.

#### Results

Ten samples of 1 + s of a Hamlin orange cultivar were evaluated, thus yielding the EO of main average composition displayed in Table 1, where data are compared with those obtained from different regions. The EO of Jujuy is more balanced with respect to the contribution of hydrocarbonated monoterpenes than those EO of other regions, but has a low percentage of linalool (1.0) compared to the others (1.6-17.6), and more citronellal (1.9).

**Table 1**. Comparative composition (%) of the petitgrain-type EO of *Citrus sinensis* (L.) Osbeck *cv*. Hamlin

SOURCE	Jujuy	Florida	Nigeria	China
sabinene	30.2	52.0-58.0	16.0-29.4	27.2
β-pynene	8.4		1.3-2.5	27.2
myrcene	9.1	3.9-6.1	1.4-3.8	4.8
<b>ర్</b> -3-carene	5.4	2.0-8.0	6.0-11.7	
<b>a</b> − terpinene	2.9	0.7-1.5		
limonene	3.8	2.3-6.4	3.7-7.4	4.6

From a total of 10 samples of 1 + s of a Dancy mandarin cultivar petitgrain was obtained. The main constituents and their average percentages are shown in Table 2. This pg differs from those of Sicily (rich in limonene) and is similar to those of Florida (Attaway *et* 

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vol 13 May-August 2007, **64-65** htt *al.*, 1963) and Israel (with phenolic notes) (Fleisher and Fleisher, 1990).

**Table 2**: Comparative composition (%) of the EO of *Citrus reticulata* Blanco *cv*. Dancy from different sources.

SOURCE	Jujuy	Sicily	Israel	Florida
p-cymene	1.5	8.2	4.1	
limonene	3.6	67.7	0.4	0.8-1.9
<b>c</b> -terpinene	10.5	9.1	3.1	4.3-10.0
linalool	35.1	0.2	50.7	52.0-78.0
thymol methyl ether	8.3		4.6	1.1-16.0
thymol	5.0		11.7	1.6-6.9

Twenty four samples of 1 + s of creole mandarin were extracted. The percentages of the main constituents of these samples were compared with those of other pg of *C. reticulata* Blanco, which share the main chemical component: methyl *N*-methylanthranilate. The results are shown in Table 3. The Balady cultivar of Israel (Fleisher and Fleisher, 1991) yields the EO of pg more similar to that of Jujuy with respect to the composition of the main constituents.

**Table 3**: Comparative composition (%) of the EO of *C. deliciosa* Ten. and *C. reticulata* Blanco from different sources.

SOURCE	Jujuy	Italia	Balady Israel	Egipto
myrcene	0.6	8.0	0.3	0-2
limonene	12.0	24.2	4.9	1-6
<b>α</b> - terpinene	19.9		12.6	
linalool	0.1	4.4	0.1	0-3
methyl N-methylanthranilate	55.3	50.1	65.7	0-6

#### Conclusions

The use of leaf material of *Citrus* cultivars from Jujuy for the EO extraction of petitgrain leads to products of interest in perfumery, cosmetics and aromatherapy. Each EO particular composition provides olfactory notes that distinguish them from those of other regions, making it usually sweeter (pg of orange), more fruity (pg of Dancy mandarin), and with aromatherapic potential (pg of Creole mandarin) because of the content of methyl *N*-methylanthranilate (Franchomme *et al.*, 1996).

Note: This study was presented at the "XXVI Congreso Argentino de Química", San Luis, Argentina, 2006

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