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# Essential oils of native and naturalized Lamiaceae species growing in the Patagonia region (Argentina)

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# Essential oils of native and naturalized *Lamiaceae* species growing in the Patagonia region (Argentina)

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**ABSTRACT**

This is the first comprehensive study of essential oils of wild aromatic *Lamiaceae* present in Patagonia, including exotic and native species. The most commonly representatives of this family in Patagonia include one species of the adventitious *Origanum vulgare* L., three naturalized mints, *Mentha rotundifolia* L., *M. pulegium* L. and *M. spicata* L. and two native species: *Clinopodium darwinii* (Benth.) Kuntze and *Scutellaria nummulariifolia* Hook. *f.* The essential oils were isolated by hydrodistillation of the aerial parts of each of these species collected during 3 years and analyzed by GC-FID-MS. The major components found were menthone (5.4–10.2%) and pulegone (78.3–89.8%) in *M. pulegium*; piperitenone oxide (75.6–68.7%) in *M. rotundifolia;* carvone (34.0–70.4%) in *M. spicata;* sabinene (2.7–5.9%), *p*-cymene (9.3–36.1%) and linalool (11.3–21.4%) in *O. vulgare;* pulegone (56.6–72.4%) in *Clinopodium darwinii;* acetophenone (19.0%) and α-terpineol (9.5%) in *Scutellaria nummulariifolia*. This is the first report on the chemical composition of the essential oil of *S. nummulariifolia*.

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## Introduction

The *Lamiaceae* family comprises numerous species that are considered aromatic plants due to their high content of essential oils. The most commonly non-cultivated representatives of the *Lamiaceae* family found in Patagonia, Argentina, include one species of oregano, *Origanum vulgare* L., three naturalized species of mint, *Mentha rotundifolia* L., *M. pulegium* L. and *M. spicata* L., and two native species, *Clinopodium darwinii* (Benth.) Kuntze and *Scutellaria nummulariifolia* Hook. *f.*

According to Zuloaga and Morrone (1) there are three *Mentha* species in Argentina (perennial and adventitious), two of them grow in the Patagonia, *Mentha spicata* L. in the provinces of Chubut, Neuquén, Río Negro, but also grows in other provinces of Argentina as Buenos Aires, Córdoba, Corrientes, Entre Ríos, Salta and Tucumán; and *Mentha pulegium* L. in the provinces of Chubut, Neuquén, Río Negro but also in the provinces of Buenos Aires, Córdoba, Entre Ríos, Jujuy, Mendoza, Misiones and Salta. Meanwhile *M. rotundifolia* and *O. vulgare* are not mentioned by these authors, probably due to their more limited presence. Besides, the same authors mention the native species *Clinopodium darwinii* (Benth.) Kuntze, which is an endemic perennial herb growing in the provinces of Chubut, Neuquén, Río Negro, Santa Cruz and Tierra del Fuego; and *Scutellaria nummulariifolia* Hook. *f.*, an endemic perennial herb growing in Chubut, Río Negro, Santa Cruz, Tierra del Fuego.

*Mentha pulegium* L. is an herbaceous species, locally known as 'poleo'. It grows wild in humid places, with a varied amount and degree of development according to climatic conditions. It is an aromatic plant traditionally used to treat dyspepsia and against intestinal cramps due to its carminative and antispasmodic properties. It is also used for the production of flavors and fragrances. Previous studies on the composition of the essential oil revealed pulegone as the major component, whose content is higher in the vegetative state and during flowering but declines during the post-flowering period. It may exceed 80% of the total composition (2).

*M. rotundifolia* is a perennial herb, stoloniferous, pubescent, 80-cm high when flourished and grows near

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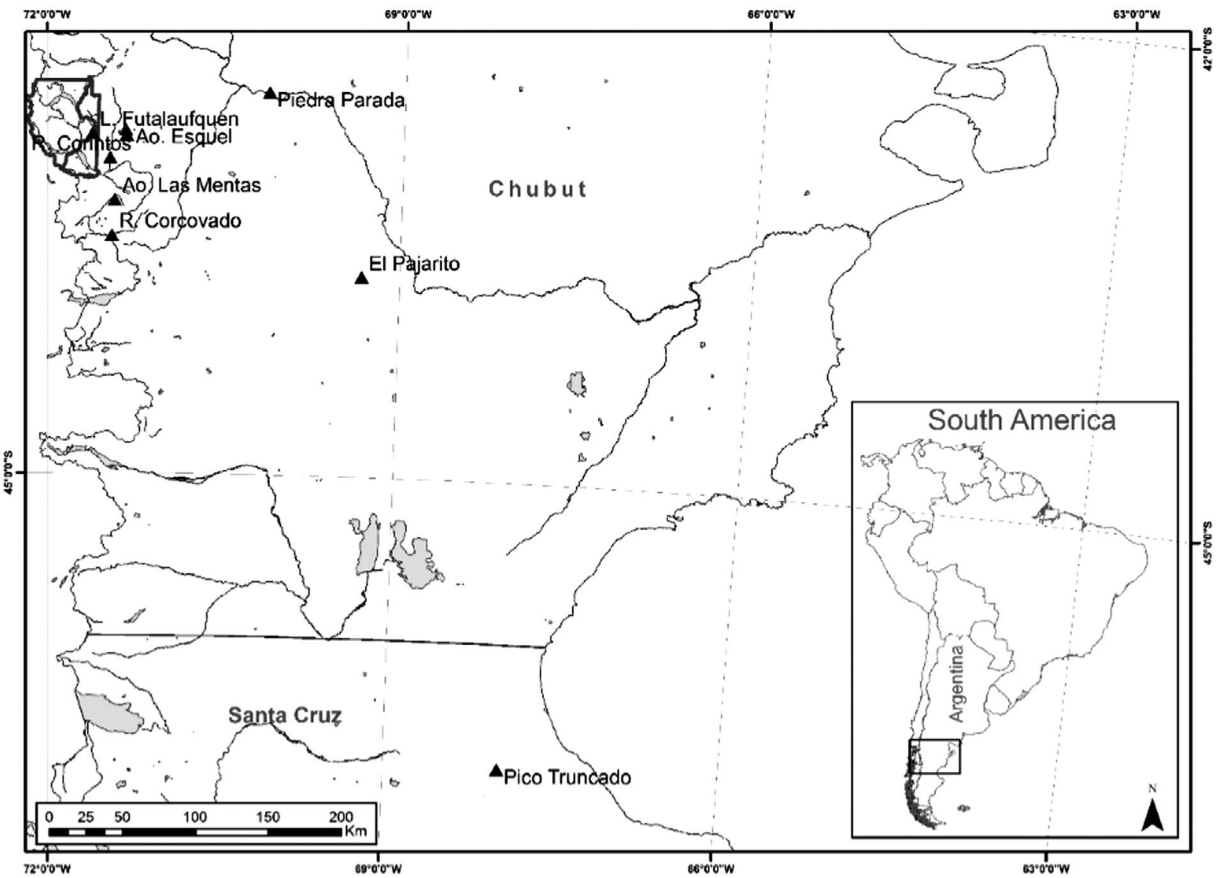


**Figure 1.** Sites of collection in the forest ecotone and steppe(west to east) in Chubut and Santa Cruz Provinces.

**Table 1.** Yield of essential oil and organoleptic characteristics of the samples analyzed.

| Species | Sites | Yield Average mL/kg | Organoleptic Characteristics |
|---|---|---|---|
| *Mentha pulegium* | Río Corinto | 23.1 | Colorless liquid, pungent, strong characteristic odor. |
| *Mentha rotundifolia* | Río Corcovado | 5.2 | Colorless liquid, light yellow, mild odor reminds of mint, bitter, a bit moldy. |
| *Mentha spicata* | Arroyo Esquel | 4.7 | Colorless liquid, mint-like odor. |
| *Mentha spicata* | Arroyo Las Mentas | 5.0 | Colorless liquid, spearmint- like odor. |
| *Mentha spicata* | Río Corinto | 5.9 | Colorless liquid, light yellow, mint-like odor. |
| *Origanum vulgare* | Lago Futalaufquen | 3.1 | Almost colorless liquid, sweet odor, pleasant, spicy. |
| *Clinopodium darwinii* | Piedra Parada | 3.9 | Colorless liquid, intense smell, reminds of thyme. |
| *Scutellaria nummulariifolia* | El Pajarito | < 0.1 | Characteristic intense herbaceous odor. |

water. It is locally known as 'white mint', 'yerbabuena' or 'hierbabuena'. *M. spicata*, 'mint' or 'hierbabuena', has a wide distribution near water streams and is the most common among the species belonging to this genus.

The oregano (*Origanum* spp.) is widely used as a flavoring, mainly in meat products and sauces and its essential oil is also used in foods as well as cosmetics and liquors. Significant morphological and chemical differences have been observed in these species, both intra-population and among cultivars.

*Clinopodium darwinii* is a native species of Patagonia (Argentina) and Southern Chile (1). It is locally known as 'pampa tea' or 'thyme' and is popularly used as infusion or syrup for digestive and liver disorders. 'Tehuelche' communities used decoctions of the plant as sudorific (3).

*Scutellaria nummulariifolia*, commonly known as 'sand flower' is a perennial herb native of Patagonia which grows from sea level to 900 m. a. s. l., from Río Negro to Tierra del Fuego (4). Except for the latter species, the others are used for medicinal purposes.

This is the first comprehensive study of the essential oils of wild aromatic *Lamiaceae* present in Patagonia, including exotic and native species, all non-cultivated. These include the analysis of the essential oil of *Scutellaria nummulariifolia*, being a native species not studied previously.

## Materials and methods

Samples of each studied species consisted of a representative collection of one population. Randomly small

**Table 2.** Chemical composition of *Mentha rotundifolia* during the years 2007–2009.

| LRIN | LRINB | LRIP | LRIPB | COMPOUND | Area % | | |
|---|---|---|---|---|---|---|---|
| | | | | | 2007 | 2008 | 2009 |
| 844 | 846a | 1240 | 1216b | *trans*-2-Hexenal | 0.3 | – | 0.3 |
| 945 | 932a | 1043 | 1025b | α-Pinene | 1.8 | 1.4 | 1.1 |
| 971 | 974a | 1448 | 1444b | Oct-3-en-1-ol | 0.2 | – | 0.1 |
| 985 | 969a | 1138 | 1122b | Sabinene | 1.2 | – | 0.8 |
| 989 | 988a | 1390 | 1392b | 3-Octanol | 2.3 | 0.9 | 1.4 |
| 992 | 988a | 1170 | 1161b | Myrcene | 1.6 | 1.0 | 1.3 |
| 994 | 974a | 1133 | 1110b | β-Pinene | 2.2 | 1.7 | 1.5 |
| 1024 | 1024a | 1221 | 1198b | Limonene | 2.8 | 2.0 | 2.6 |
| 1026 | 1026a | 1234 | 1211b | 1,8-Cineole | 2.7 | 1.7 | 2.0 |
| 1042 | 1044a | 1260 | 1250b | *trans*-β-Ocimene | 0.1 | – | 0.1 |
| 1047 | 1032a | 1235 | 1235b | *cis*-β-Ocimene | 2.3 | 0.7 | 1.6 |
| 1084 | 1085a | – | – | *p*-Mentha-2,4(8)-diene | – | – | 0.1 |
| 1110 | 1110a | – | – | Oct-3-en-1-yl acetate | 0.8 | 0.2 | 0.2 |
| 1119 | 1120a | 1378 | – | 3-Octanyl acetate | 2.2 | 1.3 | 0.6 |
| 1194 | 1195a | 1641 | 1632b | Myrtenal | 0.2 | – | 0.2 |
| 1199 | 1179a | 1855 | 1848b | *p*-Cymen-8-ol | 0.3 | 0.2 | |
| 1233 | 1232a | – | – | *cis*-3-Hexenyl 3-methyl butanoate | 0.6 | 0.4 | 0.5 |
| 1235 | 1233a | 1663 | 1655b | Pulegone | – | 1.8 | – |
| 1237 | 1238a | 1793 | 1784b | Cuminaldehyde | – | – | 0.1 |
| 1240 | 1239a | 1745 | 1734b | Carvone | – | – | 0.1 |
| 1252 | 1252a | – | – | *trans*-Piperitone epoxide (epoxide *vs*. IPP) | 0.2 | 0.2 | 0.2 |
| 1258 | 1259a | – | – | *cis*-Carvone oxide | – | 0.4 | 0.8 |
| 1370 | 1366a | 1962 | 1983b | Piperitenone oxide | 61.2 | 75.6 | 68.7 |
| 1377 | 1374a | 1511 | 1491b | α-Copaene | 0.3 | 0.4 | – |
| 1417 | 1417a | 1614 | 1599b | *trans*-Caryophyllene | 6.3 | 3.7 | 5.5 |
| 1441 | 1440a | 1668 | 1651b | *cis*-β-Farnesene | 0.3 | – | 0.3 |
| 1451 | 1452a | 1683 | 1667b | α-Humulene | 0.3 | 0.2 | 0.3 |
| 1482 | 1484a | 1721 | 1708b | Germacrene D | 7.3 | 5.3 | 8.8 |
| 1512 | 1500a | 1742 | 1735b | Bicyclogermacrene | 0.3 | – | 0.2 |
| 1515 | 1511a | 1740 | – | δ- Amorphene | 0.2 | – | 0.1 |
| 1522 | 1522a | 1763 | 1756b | δ- Cadinene | 0.2 | – | – |
| 1599 | 1577a | 2125 | 2127b | Spathulenol | 0.4 | – | – |
| 1605 | 1582a | 1989 | 1986b | Caryophyllene oxide | 0.2 | – | – |
| 1606 | 1592a | 2082 | 2090b | Viridiflorol | 0.7 | – | – |
| | | | | Total | 99.5 | 99.1 | 99.5 |

Notes: Order of elution of the non-polar column. LRIN: Experimental linear retention indices in the non-polar column; LRIP: experimental linear retention indices in the polar column; LRINB: linear retention indices in the non-polar column from bibliography; LRIB: linear retention indices in the polar column from bibliography; a: see (7); b: see (72).

portions of the aerial parts (about 10 or 20 g per plant) were taken up to a total of 500 g to 1 kg per species.

A wild *M. pulegium* population from Río Corinto was studied during the summer of 2007, 2008 and 2009. *M. rotundifolia* was collected on the coast of the Río Corcovado, near the homonymous city, during the summer of 2007, 2008 and 2009. Three sites were selected for *M. spicata*: Arroyo Esquel, Río Corinto and Arroyo Las Mentas. Samples were taken annually for three consecutive years, in the summer seasons of 2007, 2008 and 2009. The essential oils analyzed were compared with two additional materials, one experimentally cultivated in the city of Esquel and other adventitious plants collected in the Arroyo Pescado, in the Patagonian plateau. *Origanum vulgare* was obtained from a wild population during and after blooming, collected around Lake Futalaufquen, during the years 2007, 2008 and 2009. *C. darwinii* was collected in Pico Truncado, Santa Cruz Province and Piedra Parada, Chubut Province in the summer of 2007 and 2008. *S. nummulariifolia* was collected near El Pajarito (Paso de los Indios, Chubut Province) in 2009. The sites mentioned are shown in Figure 1.

Samples were collected in blooming stage. The botanical identification of plant materials was done by Ing. Pedro Guerra and voucher specimens were deposited in FI-UNPSJB-Esquel Herbarium under the numbers BF 053 to 058. The volatile fraction of each sample was isolated by hydrodistillation of the air dried plant material for 3 hours using a Clevenger apparatus (5).

Yields were calculated in mL of essential oil/kg of dried material. Essential oils were analyzed using the same equipment and methodology as described previously (6). They were carried out on a GC–FID–MS system, Perkin Elmer Clarus 500, with one injector (split ratio: 1:100) connected by a flow splitter to two capillary columns: (a) polyethylene glycol PM *ca.* 20,000 and (b) 5% phenyl–95% methyl silicone, both 60 m × 0.25 mm with 25 μm film thickness. The polar column was connected to a FID, while the nonpolar column was connected to a FID and a quadrupolar mass detector (70 eV) by a vent system (MSVent®).

**Table 3.** Chemical composition of *Mentha spicata* in the years 2006–2009, from five sites and required values for the corresponding ISO norm (19).

| LRIN | LRINB | LRIP | LRIPB | COMPOUND | A | B | C | D | E | F | G | H | I | J | ISO |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 844 | 854a | 1240 | 1216b | *trans*-2-Hexenal | – | – | – | – | – | – | – | – | 0.3 | – | |
| 945 | 932a | 1043 | 1025b | α-Pinene | 0.6 | 1.0 | 0.8 | 0.4 | 0.8 | 0.7 | 1.0 | 1.2 | 1.5 | 0.8 | |
| 985 | 969a | 1138 | 1122b | Sabinene | 0.4 | 0.8 | 0.6 | 0.3 | 0.7 | 0.5 | 0.8 | 0.5 | 1.0 | 0.5 | |
| 989 | 988a | 1390 | 1392b | 3-Octanol | 0.6 | 0.2 | – | 0.4 | 0.4 | – | – | 0.4 | 0.4 | 0.3 | 0.6 – 1.4 |
| 992 | 988a | 1170 | 1161b | Myrcene | 3.4 | 2.2 | 2.2 | 2.3 | 1.9 | 2.8 | 3.1 | 2.5 | 3.9 | 2.2 | |
| 994 | 974a | 1133 | 1110b | β-Pinene | 0.9 | 1.7 | 1.4 | 0.7 | 1.4 | 1.2 | 1.7 | 2.4 | 2.1 | 1.3 | |
| 1009 | 1008a | 1175 | 1147b | δ-3-Carene | – | – | – | – | – | – | – | 0.2 | – | – | |
| 1024 | 1024a | 1221 | 1198b | Limonene | 8.8 | 12.6 | 9.5 | 6.9 | 12.4 | 7.7 | 9.3 | 10.2 | 16.4 | 11.7 | 9.0 – 15.0 |
| 1026 | 1026a | 1234 | 1211b | 1,8-Cineole | 3.6 | 9.0 | 8.8 | 3.0 | 8.7 | 5.3 | 8.7 | 5.2 | 9.4 | 5.8 | |
| 1047 | 1032a | 1235 | 1235b | *cis*-β-Ocimene | 0.5 | – | – | 0.3 | 0.1 | – | – | 0.2 | 0.5 | 0.2 | |
| 1090 | 1095a | 1549 | 1543b | Linalool | – | – | – | – | 0.9 | – | 0.2 | – | – | – | |
| 1119 | 1120a | 1378 | – | 3-Octanyl acetate | – | 0.3 | – | 0.2 | – | 0.4 | 0.4 | – | 0.2 | – | |
| 1146 | 1148a | 1485 | 1465b | Menthone | – | – | – | – | – | – | – | – | – | – | 0 – 0.2 |
| 1160 | 1158a | 1513 | 1484b | Isomenthone | 0.6 | – | – | – | – | – | – | – | – | – | |
| 1162 | 1162a | 1674 | 1679b | δ-Terpineol | – | 0.3 | | | 0.3 | 0.2 | 0.2 | 0.2 | 0.2 | 0.2 | |
| 1190 | 1195a | 1684 | 1671b | Methyl chavicol | 0.9 | – | – | – | – | – | – | – | – | – | |
| 1197 | 1174a | 1614 | 1601b | Terpinen-4-ol | – | – | – | – | 0.2 | – | – | – | – | – | |
| 1211 | 1186a | 1705 | 1694b | α-Terpineol | 0.5 | 0.2 | – | 0.2 | 0.6 | – | 0.2 | 0.2 | 0.2 | 0.3 | |
| 1212 | 1192a | 1755 | – | Dihydrocarveol* | 0.3 | 12.2 | 16.5 | 4.5 | 2.6 | 19.9 | 17.0 | 3.5 | – | – | |
| 1214 | 1191a | 1623 | | *cis*-Dihydrocarvone | 2.4 | 0.4 | 0.4 | 1.0 | – | 0.3 | – | 0.2 | 4.8 | 0.6 | 1.0 – 2.5 |
| 1226 | 1200a | 1642 | 1623b | *trans*-Dihydrocarvone | – | – | – | – | – | – | – | – | 0.3 | – | |
| 1227 | 1215a | 1838 | 1836b | *trans*-Carveol | – | 0.7 | 0.6 | – | – | 0.9 | – | – | – | – | |
| 1233 | 1232a | – | – | *cis*-3-Hexenyl 3-Methyl butanoate | 0.6 | 0.3 | – | – | 0.4 | – | – | – | 0.2 | – | |
| 1235 | 1233a | 1663 | 1655b | Pulegone | 3.4 | – | – | – | – | 0.1 | – | – | – | – | |
| 1237 | 1226a | 1869 | 1854b | *cis*-Carveol | – | 0.3 | – | – | 0.3 | – | – | – | – | – | |
| 1240 | 1239a | 1745 | 1734b | Carvone | 67.8 | 44.1 | 43.1 | 70.4 | 64.9 | 34.0 | 44.5 | 69.6 | 52.2 | 72.5 | 60.0 – 70.0 |
| 1249 | 1249a | 1739 | 1730b | Piperitone | – | 0.7 | – | – | 0.3 | – | – | 0.3 | 0.5 | – | |
| 1258 | 1259a | – | – | *cis*-Carvone oxide | – | 0.2 | – | – | 0.2 | – | – | – | – | – | |
| 1306 | 1306a | 1646 | – | Dihydrocarvyl acetate | – | 1.0 | 1.0 | 0.3 | 0.2 | 1.4 | 0.8 | – | 0.2 | – | 0.1 – 0.6 |
| 1325 | 1326a | – | – | Isodihydrocarvyl acetate | 0.5 | 6.5 | 8.7 | 2.4 | 1.0 | 13.4 | 5.7 | 0.9 | 1.9 | – | |
| 1337 | 1339a | – | – | *trans*-Carvyl acetate | 0.3 | 2.1 | 1.6 | 0.8 | 0.4 | 2.8 | 0.9 | 0.3 | 0.3 | – | |
| 1360 | 1365a | 1781 | 1775b | *cis*-Carvyl acetate | 0.4 | 1.5 | 1.9 | 1.1 | 0.3 | 3.6 | 0.9 | 0.4 | 0.3 | – | 0.1 – 0.6 |
| 1362 | 1359a | 1729 | 1718b | Neryl acetate | – | – | – | – | 0.2 | – | – | – | – | – | |
| 1400 | 1408a | 1591 | 1588b | *cis*-Caryophyllene | – | – | – | 1.2 | – | – | – | – | – | – | |
| 1400 | 1389a | 1603 | 1591b | β-Elemene | – | – | – | – | – | – | – | – | – | 0.2 | |
| 1405 | 1387a | 1537 | 1523b | β-Bourbonene | 1.1 | 0.7 | 0.6 | 1.5 | 0.2 | 1.0 | 0.6 | 0.4 | 0.5 | 1.0 | 1.0 – 2.0 |
| 1417 | 1417a | 1614 | 1599b | *trans*-Caryophyllene | 1.4 | 0.6 | 0.9 | – | 0.5 | 0.9 | 0.6 | 0.6 | 0.6 | 1.5 | |
| 1428 | 1430a | 1591 | 1580b | β-Copaene | 0.4 | – | – | – | – | – | – | – | – | 0.3 | |
| 1605 | 1582a | 1989 | 1986b | Caryophyllene oxide | – | – | – | 0.4 | – | 0.4 | – | – | – | – | |
| 1606 | 1592a | 2082 | 2090b | Viridiflorol | | | | | | | | | | | 0.1 – 0.5 |
| | | | | Total | 99.4 | 99.6 | 98.6 | 98.3 | 99.9 | 97.5 | 96.6 | 99.4 | 97.6 | 99.4 | |

Notes: Order of elution of the non-polar column. LRIN: Experimental linear retention indices in the non-polar column; LRIP: experimental linear retention indices in the polar column; LRINB: linear retention indices in the non-polar column from bibliography; LRIB: linear retention indices in the polar column from bibliography; a: see (7); b: see (72). A: Esquel, December/06; B: Esquel, April/08; C: Esquel, February/09; D Corinto, December/08; E: Corinto, March/08; F: Arroyo Mentas, March/07; G: Arroyo Mentas, April/08; H: Arroyo Mentas, February/09; I: Esquel cultivado, February/08; J: Arroyo Pescado, dic/08. ISO: see (19); *: isomer not identified.

**Table 4.** Chemical composition of *Mentha pulegium* in the years 2007–2009 in Río Corinto.

| LRIN | LRINB | LRIP | LRIPB | COMPOUND | Area % | | |
|---|---|---|---|---|---|---|---|
| | | | | | 2007 | 2008 | 2009 |
| 945 | 932a | 1043 | 1025b | α-Pinene | 0.3 | 0.3 | 0.3 |
| 989 | 974a | 1390 | 1392b | 3-Octanol | 0.4 | 0.2 | 0.2 |
| 994 | 974a | 1133 | 1110b | β-Pinene | 0.2 | 0.2 | 0.3 |
| 1024 | 1024a | 1221 | 1198b | Limonene | 0.3 | 0.2 | 0.1 |
| 1146 | 1148a | 1485 | 1465b | Menthone | 7.6 | 5.4 | 10.2 |
| 1160 | 1158a | 1513 | 1484b | Isomenthone | 0.3 | 0.3 | 0.6 |
| 1175 | 1179a | 1673 | – | Isomenthol | 1.8 | 0.6 | 2.0 |
| 1197 | 1174a | 1614 | 1601b | Terpinen-4-ol | – | – | 0.1 |
| 1214 | 1191a | 1623 | – | *cis*-Dihydrocarvone | 1.5 | 2.0 | 1.8 |
| 1230 | 1233a | 1663 | 1655b | Pulegone | 78.3 | 89.8 | 84.0 |
| 1240 | 1239a | 1745 | 1734b | Carvone | 0.3 | – | – |
| 1252 | 1252a | – | – | *trans*-Piperitone epoxide (epoxide *vs*. IPP) | 0.7 | – | – |
| | | | | Total | 92.0 | 99.0 | 99.7 |

Notes: Order of elution of the non-polar column. LRIN: Experimental linear retention indices in the non-polar column; LRIP: experimental linear retention indices in the polar column. LRINB: linear retention indices in the non-polar column from bibliography; LRIB: linear retention indices in the polar column from bibliography; a: see (7); b: see (72).

**Table 5.** Chemical composition of *Origanum vulgare* in 2007–2009 of Lago Futalaufquen.

| LRIN | LRINB | LRIP | LRIPB | COMPOUND | Area % | | |
|---|---|---|---|---|---|---|---|
| | | | | | 2007 | 2008 | 2009 |
| 670 | 658a | – | – | 3-Methyl butanal | – | 0.1 | – |
| 785 | 785a | – | – | Butane-2,3-diol | 2.5 | 0.1 | – |
| 842 | 846a | 1240 | 1216b | *trans*-2-Hexenal | – | 0.1 | – |
| 886 | 889a | 1193 | 1182b | 2-Heptanone | 0.3 | – | – |
| 929 | 924a | 1036 | 1027b | α-Thujene | 0.5 | 1.6 | 0.6 |
| 945 | 932a | 1043 | 1025b | α-Pinene | 0.7 | 1.2 | 0.5 |
| 951 | 946a | 1100 | 1069b | Camphene | 0.7 | 0.8 | 0.3 |
| 971 | 974a | 1448 | 1444b | Oct-3-en-1-ol | 2.2 | 1.2 | 0.4 |
| 975 | 979a | 1267 | 1255b | 3-Octanone | 0.2 | 0.5 | 0.3 |
| 985 | 969a | 1138 | 1122b | Sabinene | 2.7 | 5.9 | 4.0 |
| 989 | 988a | 1390 | 1392b | 3-Octanol | 0.1 | 0.1 | 0.1 |
| 992 | 988a | 1170 | 1161b | Myrcene | 0.8 | 2.4 | 1.3 |
| 994 | 974a | 1133 | 1110b | β- Pinene | 0.4 | 0.7 | 0.5 |
| 1000 | 1002a | 1191 | 1168b | α-Phellandrene | – | – | 0.1 |
| 1010 | 1014a | 1206 | 1178b | α-Terpinene | 0.1 | 1.6 | 1.7 |
| 1015 | 1020a | 1286 | 1270b | *p*-Cymene | 34.2 | 36.1 | 9.3 |
| 1024 | 1024a | 1221 | 1198b | Limonene | 0.6 | 1.3 | 0.6 |
| 1026 | 1026a | 1234 | 1211b | 1,8-Cineole | 0.1 | 0.2 | 0.3 |
| 1042 | 1025a | 1227 | 1209b | β-Phellandrene | – | 0.1 | 0.2 |
| 1042 | 1044a | 1260 | 1250b | *trans*-β-Ocimene | 2.7 | 12.4 | 13.3 |
| 1051 | 1054a | 1264 | 1245b | γ-Terpinene | 1.1 | 11.0 | 12.4 |
| 1060 | 1065a | 1468 | 1460b | *cis*-Sabinene hydrate (IPP *vs*. OH) | 5.7 | 0.5 | 0.5 |
| 1075 | 1085a | – | – | *p*-Mentha-2,4(8)-diene | – | 0.5 | 0.4 |
| 1079 | 1084a | 1452 | 1454b | *trans*-Linalool oxide (furanoid) | 0.3 | – | – |
| 1090 | 1095a | 1549 | 1543b | Linalool | 21.4 | 11.3 | 13.4 |
| 1095 | 1098a | 1552 | 1549b | *trans*-Sabinene hydrate (IPP *vs*. OH) | 0.8 | 0.2 | 0.3 |
| 1100 | 1108a | – | – | *p*-Mentha-1,3,8-triene | 0.2 | 0.2 | 0.2 |
| 1108 | 1105c | – | – | *trans*-6-Methyl hepta-3,5-dien-2-one | 0.1 | – | 0.5 |
| 1129 | 1131a | – | – | *cis*-Myroxide | 0.2 | – | – |
| 1134 | 1136a | 1568 | 1584b | *trans*-*p*-Menth-2-en-1-ol | 0.1 | – | 0.1 |
| 1139 | 1141a | 1541 | 1515b | Camphor | 0.1 | – | – |
| 1165 | 1165a | 1711 | 1700b | Borneol | 1.3 | 0.5 | 0.2 |
| 1197 | 1174a | 1614 | 1601b | Terpinen-4-ol | 2.9 | 3.0 | 4.5 |
| 1199 | 1179a | 1855 | 1848b | *p*-Cymen-8-ol | 0.2 | – | 0.1 |
| 1211 | 1186a | 1705 | 1694b | α-Terpineol | 0.3 | 0.3 | 0.4 |
| 1240 | 1239a | 1745 | 1734b | Carvone | 0.1 | – | – |
| 1240 | 1241a | 1619 | 1599b | Carvacryl methyl ether | 0.4 | 0.2 | 0.2 |
| 1283 | 1287a | 1581 | 1579b | Bornyl acetate | 0.1 | – | – |
| 1291 | 1289a | 2195 | 2164b | Thymol | 0.2 | 0.7 | 3.8 |
| 1293 | 1298a | 2216 | 2211b | Carvacrol | 0.1 | – | 0.1 |
| 1400 | 1387a | 1537 | 1523b | β-Bourbonene | 1.2 | 0.3 | 0.8 |
| 1405 | 1408a | 1716 | 1712b | Dodecanal | – | – | 1.3 |
| 1415 | 1419a | 1576 | 1577b | β-Ylangene | 0.1 | – | 0.3 |
| 1417 | 1417a | 1614 | 1599b | *trans*-Caryophyllene | 2.2 | 1.2 | 4.7 |
| 1428 | 1430a | 1591 | 1580b | β-Copaene | 0.2 | – | 0.3 |
| 1430 | 1432a | 1596 | 1576b | *trans*-α-Bergamotene | – | – | 0.3 |
| 1451 | 1452a | 1683 | 1667b | α-Humulene | 0.3 | 0.1 | 0.5 |
| 1455 | 1458a | 1658 | 1649b | *allo*-Aromadendrene | 0.7 | 0.2 | 0.5 |
| 1498 | 1484a | 1721 | 1708b | Germacrene D | 0.3 | 0.6 | 3.7 |
| 1500 | 1495a | – | – | γ-Amorphene | – | – | 0.1 |
| 1505 | 1505a | 1754 | 1744b | *trans,trans*-α-Farnesene | – | 0.1 | 0.8 |
| 1512 | 1500a | 1742 | 1735b | Bicyclogermacrene | 0.1 | 0.2 | 1.2 |
| 1522 | 1522a | 1763 | 1756b | δ-Cadinene | 0.1 | 0.2 | 1.4 |
| 1524 | 1506a | 1736 | 1740b | *cis*-α-Bisabolene | 0.3 | 0.2 | 0.9 |
| 1555 | 1550a | – | – | *cis*-Muurol-5-en-4-α-ol | – | – | 0.2 |
| 1599 | 1577a | 2125 | 2127b | Spathulenol | 1.4 | 0.2 | 0.8 |
| 1605 | 1582a | 1989 | 1986b | Caryophyllene oxide | 5.4 | 0.5 | 1.4 |
| 1608 | 1608a | 2043 | 2047b | Humulene epoxide II | 0.3 | – | – |
| 1635 | 1639a | – | – | *allo*-Aromadendrene epoxide | – | – | 0.4 |
| 1638 | 1638a | 2171 | 2170b | Γ-Cadinol | 0.2 | – | 0.3 |
| 1640 | 1640a | 2186 | 2187b | Γ-Muurolol | 0.1 | – | – |
| 1649 | 1652a | 2233 | 2227b | α-Cadinol | 0.4 | 0.1 | 2.0 |
| 1650 | 1644a | 2198 | 2183b | Torreyol | – | – | 2.2 |
| | | | | Total | 97.7 | 98.7 | 94.7 |

Notes: Order of elution of the non-polar column. LRIN: Experimental linear retention indices in the non-polar column; LRIP: experimental linear retention indices in the polar column; LRINB: linear retention indices in the non-polar column from bibliography; LRIB: linear retention indices in the polar column from bibliography; a: see (7); b: see (72); c: see (73).

**Table 6.** Chemical composition of *C. darwinii* in 2007 and 2008, Piedra Parada (PP) and 2006, Pico Truncado (PT).

| LRIN | LRINB | LRIP | LRIPB | COMPOUND | Area % | | |
|---|---|---|---|---|---|---|---|
| | | | | | PP2007 | PP2008 | PT2006 |
| 945 | 932a | 1043 | 1025b | α-Pinene | 0.5 | 0.8 | 0.5 |
| 985 | 969a | 1138 | 1122b | Sabinene | – | 0.2 | 1.1 |
| 986 | 979a | 1267 | 1259b | 3-Octanone | – | – | 0.1 |
| 992 | 988a | 1170 | 1161b | Myrcene | 0.2 | 0.2 | 0.2 |
| 994 | 974a | 1133 | 1110b | β-Pinene | 0.5 | 1.4 | 0.8 |
| 1009 | 1008a | 1175 | 1147b | δ-3-Carene | – | 0.2 | – |
| 1015 | 1020a | 1286 | 1270b | *p*-Cymene | 1.0 | 0.8 | 2.9 |
| 1024 | 1024a | 1221 | 1198b | Limonene | 0.9 | 4.8 | 2.6 |
| 1026 | 1026a | 1234 | 1211b | 1,8-Cineole | 1.1 | 1.0 | 2.7 |
| 1051 | 1054a | 1264 | 1245b | γ-Terpinene | 0.2 | – | – |
| 1090 | 1095a | 1549 | 1543b | Linalool | 1.2 | 1.3 | 1.3 |
| 1091 | 1088a | 1638 | 1616b | Methyl benzoate | – | – | 0.2 |
| 1095 | 1098a | 1552 | 1610b | *trans*-Sabinene hydrate (IPP *vs*. OH) | – | – | 0.1 |
| 1100 | 1120a | 1378 | – | 3-Octanyl acetate | – | – | 1.2 |
| 1105 | 1106a | 1923 | 1904b | 2-Phenylethyl alcohol | – | – | 0.2 |
| 1110 | 1112a | 1464 | 1440b | *trans*-Thujone | – | – | 0.1 |
| 1115 | 1119a | 1674 | 1639b | *trans*-*p*-Mentha-2,8-dien-1-ol (OH *vs*. IPP) | – | – | 0.2 |
| 1140 | 1145a | – | – | *p*-Menth-3-en-8-ol | 0.1 | – | 0.7 |
| 1146 | 1148a | 1513 | 1465b | Menthone | 0.3 | 0.5 | 0.1 |
| 1150 | 1154a | 1657 | 1651b | Sabina ketone | – | – | 0.1 |
| 1150 | 1159a | 1501 | 1482b | Menthofurane | – | – | 0.2 |
| 1160 | 1158a | 1485 | 1484b | Isomenthone | 10.6 | 12.1 | – |
| 1183 | 1185a | – | – | 3-Decanone | 0.7 | – | – |
| 1197 | 1174a | 1614 | 1601b | Terpinen-4-ol | – | – | 0.6 |
| 1199 | 1179a | 1855 | 1848b | *p*-Cimen-8-ol | – | – | 0.1 |
| 1211 | 1186a | 1705 | 1694b | α-Terpineol | 0.5 | 0.4 | 0.7 |
| 1214 | 1191a | 1623 | – | *cis*-Dihydrocarvone | 1.3 | 1.8 | 2.7 |
| 1230 | 1232a | 1604 | 1587b | Thymyl methyl ether | | 0.1 | 2.6 |
| 1233 | 1238a | 1793 | 1784b | Cuminaldehyde | 0.5 | – | – |
| 1235 | 1233a | 1663 | 1655b | Pulegone | 72.4 | 68.8 | 56.6 |
| 1240 | 1239a | 1745 | 1734b | Carvone | – | – | 0.9 |
| 1291 | 1289a | 2195 | 2164b | Thymol | 0.7 | 0.5 | 1.0 |
| 1293 | 1298a | 2216 | 2211b | Carvacrol | 0.3 | | 0.3 |
| 1310 | 1312a | – | – | Citronellic acid | 3.3 | – | – |
| 1328 | 1330a | 1622 | – | Hexyl tiglate | 0.2 | 0.2 | – |
| 1338 | 1340a | 1927 | 1909b | Piperitenone | 1.7 | 1.5 | 0.8 |
| 1400 | 1387a | 1537 | 1523b | β-Bourbonene | – | – | 0.1 |
| 1400 | 1408a | 1591 | 1588b | *cis*-Caryophyllene | – | – | 0.6 |
| 1512 | 1500a | 1742 | 1735b | Bicyclogermacrene | 0.5 | – | – |
| 1599 | 1577a | 2125 | 2127b | Spathulenol | 0.6 | 1.0 | 6.4 |
| 1605 | 1582a | 1989 | 1986b | Caryophyllene oxide | – | – | 4.3 |
| 1635 | 1639a | – | – | *allo*-Aromadendrene epoxide | – | – | 0.4 |
| | | | | Total | 99.3 | 97.6 | 93.4 |

Notes: Order of elution of the non-polar column. LRIN: Experimental linear retention indices in the non-polar column; LRIP: experimental linear retention indices in the polar column; LRINB: linear retention indices in the non-polar column from bibliography; LRIB: linear retention indices in the polar column from bibliography; a: see (7); b: see (72).



Helium was used as gas carrier at a constant flow of 1.87 mL/min. The temperature was programmed according to the following gradient: 90–225°C at 3°C/min, and then isothermal for 15 minute. The injector and both FIDs were set at 255°C and 275°C, respectively. The injection volume was 0.2 mL. The temperature of the transference line and the ion source were 180°C and 150°C respectively; the range of masses was 40–300 Da (10 scan/s). Identification of the compounds was performed by comparison of the linear retention indexes (relative to a homologue C8–C20 alkane series) obtained in both columns, with those of reference compounds. Additionally, each mass spectra obtained was compared with those from usual electronic libraries (7, 8) and from a laboratory developed mass spectra library built up from oils of known composition. The percentage composition was achieved using the single area percentage method, without considering corrections for response factors. The lowest response obtained in both columns for each component was considered.

## Results

Yields of essential oils and their organoleptic characteristics were evaluated after the distillation of each species, as detailed in Table 1. The composition of the essential oils of *Mentha rotundifolia* analyzed, according to the year or collection, is shown in Table 2. The average yield was 5.2 mL/kg. We found piperitenone oxide (68.5%), *trans*-caryophyllene (5.2%) and germacrene D (7.1%), as average values. Table 3 shows the chemical composition

**Table 7.** Chemical composition of *Scutellaria nummulariifolia* (2009), collected in El Pajarito.

| LRIN | LRINB | LRIP | LRIPB | COMPOUND | Area% |
|---|---|---|---|---|---|
| 929 | 924a | 1036 | 1027b | α-Thujene | 1.6 |
| 930 | 924a | – | – | Cumene | 0.8 |
| 985 | 969a | 1138 | 1122b | Sabinene | 1.1 |
| 992 | 988a | 1170 | 1161b | Myrcene | 1.2 |
| 994 | 974a | 1133 | 1110b | β-Pinene | 3.1 |
| 995 | 994a | – | – | Mesitilene | 1.1 |
| 1000 | 1002a | 1191 | 1168b | α-Phellandrene | 1.0 |
| 1010 | 1014a | 1206 | 1178b | α-Terpinene | 1.1 |
| 1015 | 1020a | 1286 | 1270b | *p*-Cymene | 5.1 |
| 1024 | 1024a | 1221 | 1198b | Limonene | 3.2 |
| 1026 | 1026a | 1234 | 1211b | 1,8-Cineol | 3.3 |
| 1042 | 1025a | 1227 | 1209b | β-Phellandrene | 0.5 |
| 1042 | 1044a | 1260 | 1250b | *trans*-β-Ocimene | 1.7 |
| 1051 | 1054a | 1264 | 1245b | γ-Terpinene | 1.6 |
| 1057 | 1059a | 1668 | 1648b | Acetophenone | 19.0 |
| 1090 | 1095a | 1549 | 1543b | Linalool | 4.1 |
| 1175 | 1179a | 1787 | – | *p*-Methyl acetophenone | 1.3 |
| 1197 | 1174a | 1614 | 1601b | Terpinen-4-ol | 5.3 |
| 1211 | 1186a | 1705 | 1694b | α-Terpineol | 9.5 |
| 1291 | 1289a | 2195 | 2164b | Thymol | 1.9 |
| 1400 | 1387a | 1537 | 1523b | β-Bourbonene | 5.1 |
| 1417 | 1417a | 1614 | 1599b | *trans*-Caryophyllene | 2.2 |
| 1490 | 1493a | – | – | *trans*-Muurola-4(14),5-diene | 3.2 |
| 1515 | 1518a | – | – | endo-1-Bourbonanol | 1.8 |
| 1605 | 1582a | 1989 | 1986b | Caryophyllene oxide | 1.6 |
| 1640 | 1640a | 2186 | 2187b | Γ-Muurolol | 3.0 |
| | | | | Total | 84.4 |

Notes: Order of elution of the non-polar column. LRIN: Experimental linear retention indices in the non-polar column; LRIP: experimental linear retention indices in the polar column; LRINB: linear retention indices in the non-polar column from bibliography; LRIB: linear retention indices in the polar column from bibliography; a: see (7); b: see (72).

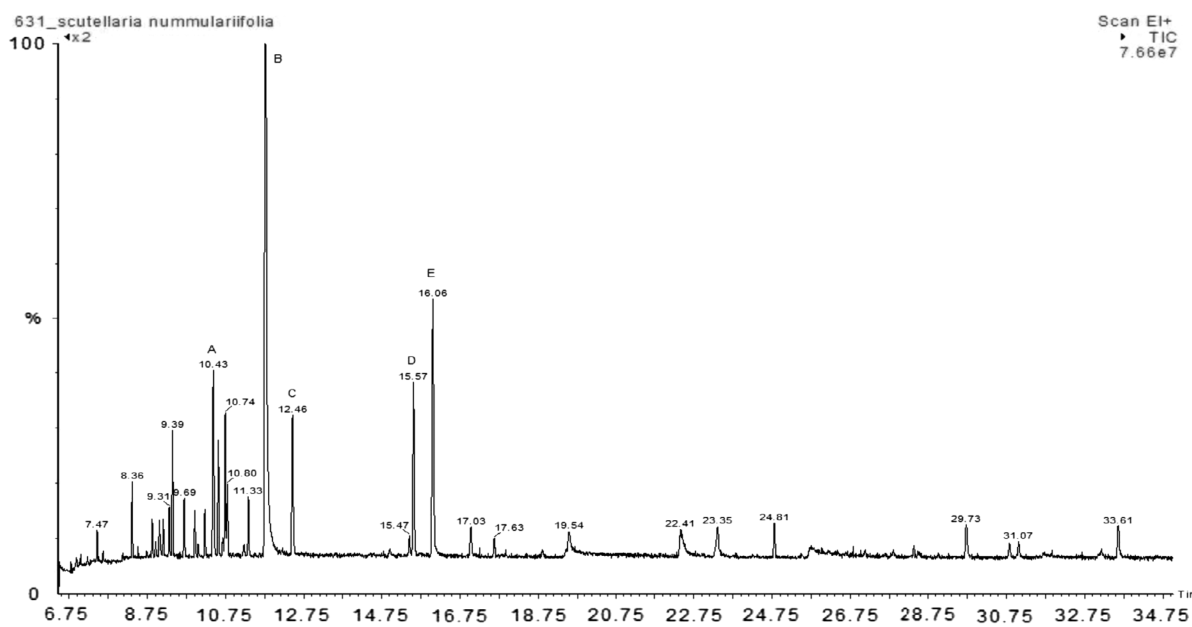


**Figure 2.** Chromatographic profile in a non-polar column of the essential oil of *Scutellaria nummulariifolia*.
Note: Major compounds identified: A= *p*-cymene, B= acetophenone, C= linalool, D= terpinen-4-ol, E= α-terpineol.

of the essential oil of *Mentha spicata* according to the place and year of collection. It had a similar yield in the three sites analyzed (about 5 mL/kg). The major component, carvone, fluctuated between 34.0% and 70.4% in the three sites and isodihydrocarvyl acetate, also varied between 0.5% and 13.4%. In the two additional materials, (Arroyo Pescado and Esquel cultivated), instead of dihydrocarveol, which was absent, limonene was detected in an appreciable percentage of 16.4% and 11.7%, depending on the location. In both cases, as in the other sites studied, the major component was carvone (52.2 and 72.5%) and the yields of 10 to 20% mL/kg. The essential oils of

**Table 8.** Principal components identified in other *Clinopodium* spp.

| Species (used part) | Principal Components | References |
|---|---|---|
| *C. ascendens*(Jord.) Samp. (now: *Clinopodium menthifolium* subsp. *ascendens* (Jord.) Govaerts.) (px) | *cis*-Isopulegone and pulegone | 32 |
| *C. darwinii* (Benth.) Kuntze (syn. *Satureja darwinii* Benth. (ns) | Piperitenone | 28 |
| *C. gilliesii* (Benth.) Kuntze (px) | Piperitenone oxide, pulegone and isopulegone | 33 |
| *C. gracile* (Benth.) Kuntze (px) | Germacrene D and nootkatone | 34 |
| *C. nubigenum* (Kunth.) Kuntze (px) | Pulegone | 35 |
| *C. odorum* (Griseb.) Harley (fl, px, st, lf) | Pulegone and piperitone oxide | 36 |
| *C. pulegium* (Rochel) Bräuchler (px) | Pulegone and menthone | 37 |
| *C. umbrosum* (M. Bieb.) Kochen (px + fl) | *cis*-Piperitone oxide | 38 |
| *C. vulgare* L (px) | Thymol and γ-terpinene | 39 |
| *C. vulgare* L (px + fl) | Vulgarone B and santolinylacetate | 40 |
| *C. vulgare* L. ssp. *arundanum* (Boiss.) Nyman (ns) | Germacrene D, *trans*-caryophyllene and caryophyllene oxide | 41 |

Note: fl: flowers; lf: leaves; ns: not specified; px: aerial parts; st: stems.

**Table 9.** Principal components found in other species of *Scutellaria* spp.

| Species (used part) | Principal Components | References |
|---|---|---|
| *S. albida* L. subsp. *albida* (px) | Linalool | 42, 43 |
| *S. albida* L. subsp. colchica (Rech.*f.*) J.R.Edm. (px) | *trans*-Caryophyllene | 43 |
| *S. albida* L. subsp. *condensata* (Rech.*f.*) J.R.Edm. (px) | Linalool, geraniol | 43 |
| *S. albida* L. subsp. *velenovskyi* (Rech.*f.*) Greuter et Burdet (px) | *trans*-Caryophyllene | 43 |
| *S. altissima* L. (ns) | Linalool | 44 |
| *S. baicalensis* Giorgi (r) | Acetophenone, palmitic acid, oleic acid | 31 |
| *S. baicalensis* Giorgi (fl) | *trans*-Caryophyllene and gremacrene D | 45 |
| *S. barbata* D. Don (px) | Oct-3-en-1-ol, menthol, methyl eugenol, linalool, hexahydrofarnesylacetone and *trans*-caryophyllene | 46, 47 |
| *S. brevibracteata* Stapf (px) | *trans*-Caryophyllene and hexahydrofarnesylacetone | 48, 49 |
| *S. californica* A. Gray (fl) | *trans*-Caryophyllene and hexahydrofarnesylacetone | 48, 49 |
| *S. X churchilliana* Fernald (ns) | *trans*-Caryophyllene, oct-3-en-1-ol, linalool, germacrene D | 50 |
| *S. diffusa* Bentham (px) | Palmitic acid, germacrene D and caryophyllene oxide | 51 |
| *S. galericulata* L. (ns) | *trans*-Caryophyllene and *trans*-β-farnesene | 52 |
| *S. grossa* Wall ex Benth. (px) | Linalool and oct-3-en-1-ol | 53 |
| *S. hastifolia* L. (px) | *trans*-Caryophyllene, germacrene D, hexahydofarnesylacetone and caryophyllene oxide | 49 |
| *S. havanensis* Jacq. (lf) | *trans*-Caryophyllene and α-humulene | 54 |
| *S. heterophylla* Montbret & Aucher ex Benth. (px) | *trans*-Caryophyllene and germacrene D | 51 |
| *S, laeteviolacea* Koidz. (px) | Oct-3-en-1-ol and germacrene D | 55 |
| *S. lateriflora* L. (px) | δ- Cadinene and calamenene | 56 |
| *S. litwinowii* Bornm. & Sint. ex Bornm. (px) | *trans*-β-Farnesene and germacrene D | 57 |
| *S. luteo-caerulea* Bornm. & Snit (lf) | *trans*-Caryophyllene and germacrene D | 58 |
| *S. multicaulis* Boiss. (px) | Linalool, *trans*-caryophyllene and caryophyllene oxide | 59 |
| *S. orientalis* L. ssp. *alpina* (Boiss.) O. Schwarz (px) | *trans*-Caryophyllene, germacrene D, hexahydofarnesylacetone and caryophyllene oxide | 49 |
| *S. orientalis* L. subsp. *alpina* (Boiss.) O. Schwarz (px) | Hexahydrofarnesylacetone, palmitic acid and *trans*-caryophyllene | 60 |
| *S. parvula* Michx. (ns) | α-Bisabolol | 52 |
| *S. pinnatifida* A. Hamilt. ssp. *alpina* (Bornm.) Rech. (px) | *trans*-Caryophyllene, germacrene D | 61 |
| *S. pinnatifida* A. Hamilt. subsp. *mucida*(Stapf) Rech. *f.* (px) | Germacrene D and spathulenol | 62 |
| *S. pinnatifida* A. Hamilt. subsp. *pinnatífida* (px) | Methyl chavicol | 63 |
| *S. repens* Buch-Ham. ex D. Donen (px) | Aromadendrene and β-funebrene | 64 |
| *S. rupestris* Boiss. et Heldr. ssp. adenotricha (Boiss. et Heldr.) (px) | Linalool and *trans*-caryophyllene | 65 |
| *S. rubicunda* Hornem. subsp. *linnaeana* (Caruel) Rech. | Linalool | 66 |
| *S. salviifolia* Benth. (px) | *trans*-Caryophyllene, germacrene D and bicyclogermacrene | 51 |
| *S. scandens* D. Don (px) | *trans*-Caryophyllene, germacrene D | 67 |
| *S. sieberi* Bentham (px) | Linalool and *trans*-caryophyllene | 65 |
| *S. utriculata* Labill. (px) | Linalool, 4-vinylguaiacol, α-terpineol, *trans*-nerolidol and geraniol | 60 |
| *S. volubilis* (Kunth) (px) | *trans*-Caryophyllene, α-humulene, germacrene D | 68 |
| *S. wightiana* Benth. (px) | β-Farnesene, 2,5-dimethyl hydroquinone | 69 |

Note: fl: flowers; lf: leaves; ns: not specified; px: aerial parts; r: roots.

*Mentha pulegium* collected in different years are detailed in Table 4. The yield of essential oils averaged 23 mL/kg, although a considerable variation was observed over the years studied (15 mL/kg to 29 mL/kg). A significant fluctuation was determined in the major component, pulegone, which was found in 78.3% to 89.8% of the total composition. Table 5 shows the constituents of the essential oils of *Origanum vulgare* analyzed in 2007–2009. The population of *O. vulgare* studied had an average yield of 3 mL/kg and the major components identified were monoterpenoids: sabinene (4.2%), *p*-cymene (26.5% on average, though varying widely: 9.3% to 36.1%), *trans*-β-ocimene (2.7–13.3%), γ-terpinene (1.1–12.4%) and linalool (11.3–21.4%). Table 6 describes the chemical composition of the essential oils of *Clinopodium darwinii* analyzed between 2007 and 2008 in Piedra Parada (PP) and 2006 in Pico Truncado (PT). The essential oils yield of *C. darwinii* was significantly higher in Pico Truncado (PT) (15 mL/kg) compared to that obtained in Piedra Parada (PP) (4 mL/kg). The major component in both sites was pulegone, 71% (PP) and 57% (PT). Isomenthone (11%) was found exclusively in the site PP and caryophyllene oxide (4.3%) was found only in the site PT.

Finally, Table 7 shows the identified components of the essential oil of *Scutellaria nummulariifolia* and Figure 2 shows its chromatographic profile. Acetophenone was the main compound found (19%).

## Discussion and conclusions

The existence of chemotypes is a common feature in most of the species and hybrids of the genus *Mentha* (9). *Mentha pulegium* has several chemotypes, the most common is known as '*pennyroyal*'. According to Lawrence (2) the main components are limonene (0.1–3.5%), 3-octanol (0.5–3.0%), menthone (1.5–8.0%), isomenthone (1.0–10.0%), pulegone (50.0–80.0%) and piperitenone (0.5–3.5%).

The yield of essential oils of *M. pulegium* was much higher than the 10 mL/kg reported by Boukhebti et al. (10) and similar to that reported by Sardashti and Adhami (11) and Ouakouak et al. (12). The great variability observed in the major component, pulegone, may be attributed to climatic conditions in the different years, particularly because of the drought that occurred in the previous sampling period in 2008, obtaining the highest yield of essential oil but the lowest percentage of pulegone.

According to the literature, *Mentha rotundifolia,* has a yield of 2 to 10 mL/kg and also presents different chemotypes, as piperitone oxide/piperitenone oxide (19.7–31.4% and 27.8–29.4%), piperitenone/piperitenone oxide (54.9–17.6%), *cis*/*trans*-dihydrocarvone (68.9–12.2%), carvone/*cis*-dihydrocarvone (60.0–10.8%), piperitenone oxide (74.2–77.4%) (13–17). In our study, the major components indicate that it is similar to the chemotype reported by Kokkini (14) and particularly similar to the one described by Lorenzo et al. (15) for the species in Uruguay, who reported the piperitenone chemotype (80.8%) and minor amounts of *trans*-caryophyllene (0.4%) and germacrene D (0.6%).

*M. spicata* grows almost worldwide and is one of the most polymorphic species in the plant kingdom (18). There is a report indicating that there are numerous chemical forms (2), and a typical American spearmint composition would be myrcene (2.5–5.0%), limonene (6.5–11.5%), *cis*-dihydrocarvone (1.5–8.5%) and carvone (55.0–68.5%).

The materials of *Mentha spicata* harvested in December during 2 years had a distinctive profile, in agreement with those proposed by the ISO norm (19) for 'native' spearmint, so these specimens could be used for the development of commercial crops.

From the analysis of the composition of the essential oils of *M. spicata* obtained at different times of the summer-autumn, a tendency was seen with lower percentages of dihydrocarveol and higher of carvone at flowering, during December–February, compared with these components during post-flowering, in March–April. In general, comparing all the samples, an inverse relationship between the percentages of these two components was observed and the sum of both is relatively constant representing the 63–75% of the total components.

According to the literature (2), the materials studied of *Mentha spicata* may correspond to *M. spicata* cv. *Neerkalka,* which yields 9 mL/kg and is rich in carvone (72%) and limonene (10%). It is noteworthy that these sites, Arroyo Esquel and the domestic cultivation, are very close (about 2 km apart). These materials are identical in appearance, but differ in the chemical composition of the essential oils, the former has dihydrocarveol and the latter has limonene as second major component.

The essential oil of *Origanum vulgare*, in its subspecies and varieties, is usually made up of representatives of one or two of these four biochemical groups, cymyl derivatives (*p*-cymene, thymol, carvacrol, γ-terpinene, etc.), sabinyl compounds (sabinene, *cis*- and *trans*-sabinene hydrate, etc.), acyclic monoterpenoids (geraniol, linalool and β-mircene) and type bornane (borneol, camphor, camphene) (20, 21).

The high content of linalool found in *O. vulgare* characterizes some materials studied by other authors (22, 23). The latter terpene is then used as an element for evaluation of possible chemotypes in *Origanum* (24–26). This type of oregano has not been found by other authors in Argentina (27–29). In our case, a great variability in the chemical composition between the years studied was observed. During 2007 and 2008 (post-blooming) the main components were *p*-cymene and linalool, whereas in 2009 (blooming) they were *p*-cymene, *trans*-β-ocimene, γ-terpinene and linalool.

The genus *Clinopodium* comprises twelve species; most of them are original from the American continent. In Argentina, nine species of *Clinopodium* are recognized, being *C. darwinii* (synonym: *Satureja darwinii* Benth.) the only one growing in Patagonia. Other authors have found the following major components for these species, as it is summarized in Table 8.

The major component found in both sites studied was pulegone, as it occurs in some other species of this genus (See Table 8).

These results found in *C. darwinii* differed from the two other reports on this essential oil. The first was carried out with material from Southern Chile (identified as *Satureja darwinii*) and the main component found was piperitenone, although the overall composition was similar to that found in this study, suggesting that they belong to the same chemotype where the series of monoterpenic *p*-menthanes are dominating (30). The second study corresponds to the analysis of the essential oil obtained from plants from Comandante Piedrabuena city, another site belonging to the Province of Santa Cruz, where the major components reported were thymol, linalool and spathulenol (31). The latter material would belong to other chemotype, with a higher content of aromatic *p*-menthanes (30).

The *Scutellaria* genus is represented by 350 species, mostly distributed in the northern hemisphere, being one of the largest genera within the *Lamiaceae* family (32). In Argentina, eight species are recognized, but *S. nummulariifolia* is the only one growing in Patagonia. No previous studies were found on the chemical composition of its essential oil, although there are numerous studies on other species of this genus with a notable variation in their principal components (Table 9). In most of these species, the main components are *trans*-caryophyllene, germacrene D, linalool and oct-3-en-1-ol. Acetophenone, the main compound found in *S. nummulariifolia,* has also been detected in ten other species of this genus at a low percentage (0.1 to 3%) but it is the major constituent in the roots of *S. baicalensis*, which is the most studied and used species in the traditional medicine (33). The other two main compounds in this species are two fatty acids, palmitic and oleic acids. Even though the material was distilled for 3 hours, no fatty acids were detected in our sample from the aerial parts.

In line with literature data indicating that the volatile content of the genus *Scutellaria* ranges between 0.8 and 3 mL/kg, the Patagonian species were also found to have a very low content of essential oil, at least in the blooming stage, a moment at which the sample collection was carried out. In general, the species belonging to this genus have very complex and varied composition of essential oils. This work is the first report on the chemical composition of essential oil of *S. nummulariifolia.*

This study is a contribution to the knowledge of the aromatic natural resources of the Patagonia region with potential medicinal and aromatic interest, and allows improving the selection of the best materials for reproduction and cultivation.

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## Disclosure statement

No potential conflict of interest was reported by the authors.

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