

## Investigación

Phytochemical Investigation of Four *Teucrium* Species

Maurizio Bruno,<sup>1</sup> Franco Piozzi,<sup>1\*</sup> Sergio Rosselli,<sup>1</sup> Antonella Maggio,<sup>1</sup> Meri Alania,<sup>2</sup> Kaddour Lamara,<sup>3</sup> Malik R.Y.Al-Hillo,<sup>3</sup> and Orietta Servettaz<sup>4</sup>

<sup>1</sup>Dipartimento di Chimica Organica, Università di Palermo, Viale delle Scienze, Parco d'Orleans II, 90128 Palermo, Italy.  
Tel +39-091-596905; Fax +39-091-596825; E-mail bruno@dicpm.unipa.it

<sup>2</sup>Georgian Academy of Sciences, Institute of Pharmacocchemistry, 36 P.Sarajishvili, Tbilisi, Georgia

<sup>3</sup>Chemistry Department, Science Exact Institute, Oum El Bouaghi University, Oum El Bouaghi 04000, Algeria

<sup>4</sup>Dipartimento di Biologia, Università di Milano, Milano, Italy

Recibido el 27 de abril del 2004; aceptado el 28 de mayo del 2004

**Abstract.** Aerial parts of four species of *Teucrium* were investigated. Three of them contain some already known neoclerodane diterpenoids, occurring in other species of *Teucrium*. Singularly, the fourth species is devoid of such products.

**Keywords:** *Teucrium*, Lamiaceae, diterpenes, neoclerodanes.

The aerial parts of species of the genus *Teucrium*, Lamiaceae (Labiatae), are known to contain neoclerodane diterpenoids showing interesting antifeedant activity. The chemistry of the diterpenoids isolated from this genus was reviewed in previous papers [1-4]. Continuing our chemotaxonomic studies on the genus, we report here on the results obtained on four more species: *T. dunense* Sennen (from Majorca island, Spain), *T. nuchense* C. Koch (from Georgia, Caucasus), *T. cylindraceum* Greuter et Burdet (from Algeria), *T. thymoides* Pomel (from Algeria).

From *T. dunense* we isolated three already known neoclerodanes: 19-acetyl-gnaphalin [5] **1**, isoeroicephalin [6] **2**, 6-acetyl-picropolin [7] **3**.

Only one known product occurred in *T. nuchense*, teucrin A [8-10] **4**.

Two known diterpenoids were identified in *T. cylindraceum*: auropolin [11] **5** and 20-epi-auropolin [12] **6**.

No diterpenoid was found in *T. thymoides*. This absence is rather unusual: including this case, the species of *Teucrium* devoid of neoclerodanes are only 14 out of the almost 120 taxa examined until now. From the taxonomic point of view, it is remarkable that 7 of them grow in the Iberian Peninsula (*T. algarbiense*, *T. compactum*, *T. lusitanicum*, *T. pseudochaetophytis*, *T. rotundifolium*, *T. scordioides*, *T. subtrifidum*), 5 in Northern Africa (*T. apollinis*, *T. cyrenaicum*, *T. davaeanum*, *T. decipiens*, *T. thymoides*), and only two in the extreme Eastern Mediterranean area (*T. cyprium*, *T. montbretii* subsp. *pamphilicum*).

## Experimental section

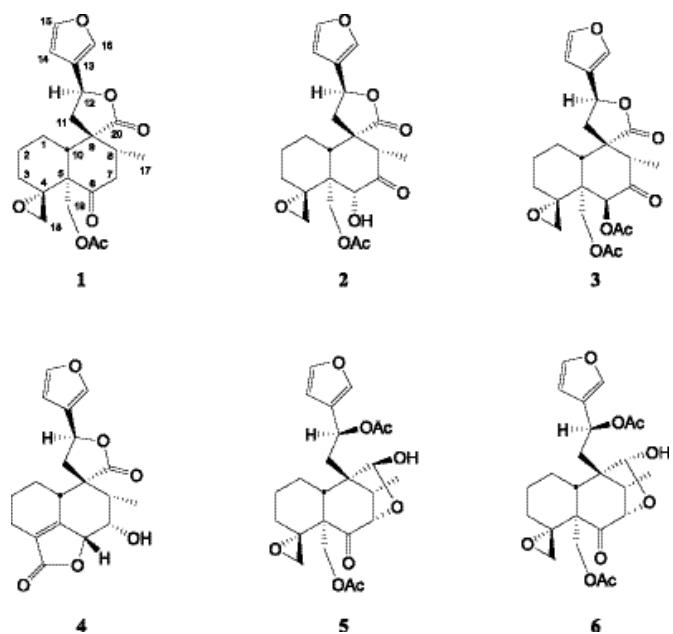
General experimental procedures. Column chromatography was performed using Merck Si gel (No. 7734). NMR spectra

**Resumen.** Las partes aéreas de cuatro especies *Teucrium* fueron estudiadas. Tres de ellas contienen algunos diterpenoides neoclerodánicos ya conocidos, que se encuentran en otras especies de *Teucrium*. Sorprendentemente, en la cuarta especie no se encuentran dichos productos.

**Palabras clave:** *Teucrium*, Lamiaceae, diterpenos, neoclerodanos.

were run on a Bruker AC 250 E apparatus. MS were recorded on a Finnigan TSQ70 instrument (70 eV, direct inlet).

**Plant material.** Aerial parts of *T. dunense* were collected on 4-6-1989 in the island of Majorca (Spain) on the dunes of Alcudia (east coast). A specimen is deposited in the Herbarium of the Dipartimento di Biologia, Università di Milano. *T. nuchense* was cultivated in the Botanic Garden of Tbilisi, Georgia, and harvested on 5-11-1998. A specimen is deposited in the Herbarium of the Botanic Garden. *T. cylindraceum* was collected on 28-4-2000 at Elmegiar, 120 km



southeast of Biskra, Algeria. A specimen is deposited in the Herbarium of the Institut National de Agronomie (INA) at El-Harrach, Algeria. *T. thymoides* was harvested on 5-5-2000 at Jebel Boukadra, 30 km North of Tebessa, Algeria. A specimen is deposited in the same Herbarium.

**Extraction and isolation.** Dried and finely powdered aerial parts of each species (about 200 g) were extracted three times with Me<sub>2</sub>CO at room temperature for 1 week. After filtration, the solvents were evaporated under reduced pressure and the residues chromatographed with a solvent gradient from 100% petroleum ether (bp 50-70°C) to 100% EtOAc, and finally with EtOAc-MeOH (9:1). Previous known compounds were identified by NMR and mass spectra, in comparison with authentic specimens.

## References

1. Piozzi, F. *Heterocycles* **1981**, *15*, 1489-1503.
2. Piozzi, F.; Savona, G; Rodriguez, B. *Heterocycles* **1987**, *25*, 807-841.
3. Piozzi, F. *Heterocycles* **1994**, *37*, 603-626.
4. Piozzi, F.; Bruno, M.; Rosselli, S. *Heterocycles* **1998**, *48*, 2185-2203.
5. Savona, G.; Paternostro, M. P.; Piozzi, F.; Rodriguez, B. *Tetrahedron Lett.* **1979**, 379-382.
6. Fayos, J.; Martinez-Ripoll, M.; Paternostro, M.P.; Piozzi, F.; Rodriguez, B.; Savona, G. *J. Org. Chem.* **1979**, *44*, 4992-4994.
7. Brieskorn, C. H.; Pfeuffer, T. *Chem. Ber.* **1967**, *100*, 1998-2010.
8. Popa, D. P.; Reinbold, A. M. *Khim. Prirod. Soedin.* **1972**, *8*, 67-69.
9. Popa, D. P.; Reinbold, A.. M. *Khim. Prirod. Soedin.* **1973**, *9*, 31-35.
10. Popa, D.P.; Reinbold, A. M., Rezvukhin, A. I. *Khim. Prirod. Soedin.* **1973**, *9*, 169-175.
11. Eguren, L.; Perales, A.; Fayos, J.; Savona, G.; Paternostro, M.P., Piozzi, F.; Rodriguez, B. *J. Org. Chem.* **1981**, *46*, 3364-3367.
12. Bruno, M.; Maggio, A. M.; Piozzi, F.; Puech, S.; Rosselli, S.; Simmonds, M. S. *J. Biochem. Syst. Ecol.* **2003**, *31*, 1051-1056.