Iridoids from *Putoria calabrica*

Rosa Tundis a, Brigitte Deguin b, Francesco Menichini a, François Tillequin b, *

a Dipartimento di Scienze Farmaceutiche dell’Università degli Studi della Calabria, I-87030 Arcavata di Rende, CS, Italy

b Laboratoire de Pharmacognosie de l’Université René Descartes, U.M.R./C.N.R.S. No. 8638, Faculté des Sciences Pharmaceutiques et Biologiques, 4, Avenue de l’Observatoire, F-75006 Paris, France

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1. Subject and source

The genus *Putoria* Pers. (Rubiaceae) only includes two species. *Putoria calabrica* (L. f.) Pers. is an undershrub widely distributed on the mountain slopes of the Mediterranean area (Ball, 1976, p. 3; Ehrendorfer, 1982, p. 353). Aerial parts were collected in Frascineto (Consenza, Italy) in July 2000. A voucher specimen has been retained at the Herbarium of the Muséum National d’Histoire Naturelle, Paris, France, under the reference P 00219924.

2. Previous work

Previous investigations of the aerial parts resulted in the isolation of phytol and β-sisterol, of several anthraquinones, and of naphthalene-derived pigments belonging to the lapachenol and tectol series (Gonzalez et al., 1974, 1977). No previous chemical work dealing with terpenoid glycosides has been recorded on the genus *Putoria*.

* Corresponding author. Fax: +33-1-40-46-96-58.
E-mail address: tillequi@pharmacie.univ-paris5.fr (F. Tillequin).

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3. Present study

Fresh aerial parts of *Putoria calabrica* (1.6 kg) were extracted with MeOH (3×5 l) at room temperature. The combined MeOH solutions were concentrated to 450 ml under reduced pressure. Upon cooling, a white solid precipitated and was separated by filtration. Crystallization in EtOAc afforded ursolic acid (7.10 g), m.p. = 284–286°C, whose structure was deduced from its spectral data and those of its methyl ester (IR, MS, and 1H NMR), identical to those previously published (Huneck and Tümmler, 1968; Seo et al., 1975a, b). The MS, IR, and 13C NMR spectral data of free ursolic acid, which were not previously described, are reported below.

The MeOH filtrate was evaporated to dryness (116 g) and an aliquot of the residue (7 g) was subjected to repeated flash column chromatography over silica gel (20–45 µm), to afford five known iridoid glycosides: asperuloside (481 mg), paederoside (126 mg), asperulosidic acid (30 mg), 3-methoxy-3,4-dihydroasperuloside (v, iridoid) (13 mg), and geniposide (8 mg). The structures of the compounds were determined on the basis of the spectral data (UV, IR, MS, 1H NMR, and 13C NMR) of both natural and peracetylated glycosides, identical with those previously described (Bailleul et al., 1977; Inouye et al., 1969; Suzuki et al., 1993; Bianco et al., 1978; Sainty et al., 1981; Böjthe-Horváth, 1982; Endo and Taguchi, 1973; Jensen, 1983).

3.1. Ursolic acid

DIC-MS m/z 474 [M+NH4]+, 457 [M+H]+, 248, 204, 191.; IR (KBr) 3518, 3442, 2927, 2871, 1715, 1697, 1457, 1387. 13C NMR (75 MHz, DMSO-d-6) δC 179.3 (C-28, s), 139.2 (C-13, s), 125.6 (C-12, d), 77.9 (C-3, d), 55.8 (C-5, d), 53.4 (C-18, d), 48.1 (C-9, d), 47.9 (C-17, s), 42.7 (C-14, s), 40.1 (C-8, s), 39.55 (C-19, d), 39.5 (C-20, d), 39.4 (C-4, s), 39.3 (C-22, t), 37.6 (C-10, s), 37.4 (C-1, t), 33.7 (C-7, t), 31.2 (C-21, t), 29.3 (C-23, q), 28.6 (C-15, t), 28 (C-2, t), 24.8 (C-16, t), 24.3 (C-27, q), 23.9 (C-11, t), 22.1 (C-30, q), 19 (C-6, t), 18 (C-26, q), 17.9 (C-25, q), 17.1 (C-29, q), 16.2 (C-24, q).

4. Chemotaxonomic significance

Iridoid glycosides, particularly asperuloside, asperulosidic acid, and geniposide, are good chemotaxonomic markers of the Rubiaceae family (Jensen et al., 1975). Paederoside is a much more interesting asperuloside derivative, due to its sulfur containing structure. It had been only isolated until now from species of *Paederia (Paederia scandens and Paederia foetida; Inouye et al., 1969; Suzuki et al., 1993)* and is described here for the first time in another Rubiaceous genus. It should be emphasized that *Paederia* is classified in tribe Paerderiae and *Putoria* in the tribe Anthospermeae, both belonging to the same Rubioideae subfamily of the Rubiaceae (Bremekamp, 1966).
References

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