B105 Iridoids from *Putoria calabrica* (Rubiaceae)

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The genus *Putoria* Pers. (Rubiaceae) only includes two species. *Putoria calabrica* (L. f.) Pers. is a undershrub widely distributed on the mountain slopes of the Mediterranean area.

Previous investigations of the aerials parts resulted in the isolation of phytol and β-sitosterol, of several anthraquinones and of naphtalene-derived pigments belonging to the lapachenol and tectol series (1). No previous chemical work dealing with terpenoid glycosides has been recorded on the genus *Putoria*.

In the course of searching for cytotoxic, hypotensive agents from medicinal herbs, fresh aerial parts of *P. calabrica* were extracted with MeOH (3x5 L) at room temperature. The methanol extract, after separation by filtration of a white solid precipitated and crystallized in EtOAc (ursolic acid), was subjected to repeated flash column chromatography over silica gel to afford five known iridoid glycosides: asperuloside, paederoside, asperulosidic acid, 3-methoxy-3,4-dihydroasperuloside (V3 iridoid) and geniposide.

The structures of the compounds were determined on the basis of the spectral data (UV, IR, MS, ^{1}H NMR and ^{13}C NMR) of both natural and peracetylated glycosides, identical with those previously described (2-5).

Iridoid glycosides, particulary asperuloside, asperulosidic acid and geniposide, are good chemotaxonomic markers of the Rubiaceae family (6).

Paederoside is a much more interesting asperuloside derivative, due to its sulfur containing structure. Previously, it had been only isolated from species of *Paederia* (*P. scandens* and *P. foetida*).

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B106 New guaianolides from *Tanacetum fruticulosum* Ledeb.

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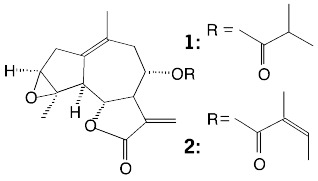
Sesquiterpene lactones have been reported to have multiple biological effects including cytotoxic, antibacterial, anti-inflammatory, hypotensive and many others. The guaianolides represent one of the largest groups of sesquiterpene lactones covering over 600 known naturally occurring compounds. Much attention has been paid to the antitumor properties associated with their cytotoxicity. The genus *Tanacetum*, with ca. 200 species, is distributed over Europe and West Asia.

As a part of our continuing studies on Iranian plants, we examined *T. fruticulosum*, collected in the Hamedan area, N. West of Iran in 1998, and isolated two new guaianolide sesquiterpene lactones (**1**,**2**) by extraction and chromatographic procedures. The air-dried aerial parts (500 g) were extracted with $CHCl_3$. The extract obtained was defatted with MeOH and first separated by CC (silica gel). The fractions obtained with Et_2O-Petrol (1:3) were separated by prep. TLC (silica gel) affording a mixture which was further separated by HPLC (RP-8, MeOH-H_2O; 7.5:2.5) to give 8 mg **1** and 12 mg **2**. The molecular formula of **1** $C_{19}H_{24}O_5$ and **2** $C_{20}H_{24}O_5$ were deduced from high resolution EIMS. With ^{1}H-NMR signals ($CDCl_3$, 500MHz), ^{13}C-NMR ($CDCl_3$) and using 2D-NMR spectroscopy, (^{1}H,^{1}H-COSY, ^{1}H,^{13}C-COSY HMQC), we were able to assign all the ^{1}H and ^{13}C chemical shifts. The observed NOEs support the proposed stereochemistry.



Reference: 1. Weyerstahl, P. et al. (1999) Flavour Fragr. J., 14,112-120.