

## SESQUITERPENE LACTONES AND FLAVONOIDS FROM *Anthemis ruthenica* GROWING WILD IN SERBIA

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The genus *Anthemis* L. (the largest genus in Asteraceae) comprises more than 210 species widespread in Europe, Asia, North Africa, East Africa (one species) [1]. About 130 species are distributed over the Mediterranean region, and nine of them can be found in Serbia [2].

Previous phytochemical work on *A. ruthenica* o. M. Bieb. revealed polyacetylenes in roots [3] and cytotoxic sesquiterpene lactones and flavonoids in the aerial parts [4]. The essential oils from *A. ruthenica* collected at Deliblatska Pescara (Deliblato Sand), Serbia have been examined previously [5]. In continuation of the study of *A. ruthenica* from the same locality, a crude extract (petroleum ether–Et<sub>2</sub>O–MeOH 1:1:1) of the air-dried aerial parts (collection 1), following the usual procedure for isolation of sesquiterpene lactones [6], was prepared. A combination of silica gel CC and preparative TLC yielded seven sesquiterpene lactones, i.e., germacranolides **1**, **6**, and **7** and eudesmanolides **2–5**, and flavonols **8** and **9**.

The isolated compounds were identified by comparison of their spectral data with those reported for tanacin (**1**) [7], desacetyl- $\beta$ -cyclopyrethrosin (**2**) [8], 1 $\beta$ ,4 $\alpha$ ,6 $\alpha$ -trihydroxyeudesm-11-en-8 $\alpha$ ,12-olide (**3**) [9], chrysanin (**4**) [10], tanapsin (**5**) [11], 3 $\beta$ -hydroxycostunolide (hanfillin or 3-*epi*-tamaulipin-B) (**6**) [12], ridentin (**7**) [13], centaureidin (**8**) [14], and penduletin (**9**) [15]. Whereas **1**, **4**, **6**, and **8** were reported recently as the constituents of *A. ruthenica* from Hungary [4], compounds **3**, **5**, **7**, and **9** were not found before in the genus.

Eudesmanolides **4** and **5** are most probably obtained via cyclization of germacranolide **1**, involving acid-catalyzed 1,10-epoxyde ring opening (Markovnikov type) followed by the well-known transannular attack of C-5 at C-10 [16].

In order to check whether the sesquiterpene lactones are accumulated on the external surface of the investigated plant, which is related to the plant's defense against predator, the repeated investigation of *A. ruthenica*, collected the following year at the same locality and at the same time as before (collection 2), was undertaken. The extract was obtained by washing of the intact fresh aerial parts with CH<sub>2</sub>Cl<sub>2</sub> and evaporating the solvent. PMR spectroscopy, using the pure isolated standards to monitor the main constituents, revealed lactones **1** and **4** as the major components of the surface extract.

**Plant Material.** *Anthemis ruthenica* M. Bieb. was collected during the flowering period in June 2002 (collection 1) and June 2003 (collection 2) in Deliblatska Pescara (Deliblato Sand) in south Banat (Vojvodina, Serbia). A voucher specimen (AR26052002) was deposited in the Herbarium of the University of Belgrade, Faculty of Biology.

**Spectral Measurements.** NMR spectra were recorded in CDCl<sub>3</sub> with TMS as internal standard using Varian Gemini 2000 (<sup>1</sup>H 200 MHz, <sup>13</sup>C 50 MHz) and Bruker AMX-500 (<sup>1</sup>H 500 MHz, <sup>13</sup>C 125 MHz) instruments. Mass spectra were obtained on a Finnigan MAT 8230 (EI, 70 eV and DCI, 150 eV, isobutane). IR spectra were measured on a Perkin–Elmer FTIR spectrometer 1725X. UV spectra were measured on a Cintra 40 spectrometer.

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## REFERENCES

1. K. Bremer, *Asteraceae Cladistics and Classification*, Timber Press, Portland, Oregon, 1994.
2. M. Gajic, *Flore de la Republique Socialiste de Serbie VII* (in Serbian), Ed. M. Josifovic, Academie Serbe des Sciences et des Artes, Belgrade, 1975, pp. 83–89.
3. L. Christensen, *Phytochemistry*, **31**, 7 (1992).
4. Y. Hajdu, I. Zupko, B. Rethy, P. Forgo, and J. Hohmann, *Planta Med.*, **76**, 94 (2010).
5. Lj. Vujisic, I. Vuckovic, V. Tesevic, D. Dokovic, M. S. Ristic, P. Janackovic, and S. Milosavljevic, *Flavour Frag. J.*, **21**, 458 (2006).
6. F. Bohlmann, C. Zdero, R. M. King, and H. Robinson, *Phytochemistry*, **23**, 1979 (1984).
7. A. I. Yunusov, N. D. Abdullaev, S. Z. Kasymov, G. P. Sidyakin, and M. R. Yagudaev, *Khim. Prir. Soedin.*, 170 (1976).
8. F. Bohlmann, A. Adler, J. Jakupovic, R. M. King, and H. Robinson, *Phytochemistry*, **21**, 1349 (1982).
9. N. Goren, A. Ulubelen, and C. Bozok-Johansson, E. Tahtsakal, *Phytochemistry*, **33**, 1157 (1993).
10. R. W. Doskotch and F. S. El-Feraly, *Can. J. Chem.*, **49**, 2103 (1971).
11. A. I. Yunusov, S. Z. Kasymov, and G. P. Sidyakin, *Khim. Prir. Soedin.*, 309 (1976).
12. V. A. Tarasov, N. D. Abdullaev, S. Y. Kasymov, and G. P. Sidyakin, *Khim. Prir. Soedin.*, 263 (1976).
13. M. A. Irwin and T. A. Geissman, *Phytochemistry*, **12**, 871 (1973).
14. C. Long, P. Sauleau, B. David, C. Lavaud, V. Cassabois, F. Ausseil, and G. Massiot, *Phytochemistry*, **64**, 567 (2003).
15. L. -K. Sy and G. D. Brown, *Phytochemistry*, **48**, 1207 (1998).
16. N. H. Fischer, E. J. Olivier, and H. D. Fischer, in: *Fortschritte der Chemie Organischer Naturstoffe* [in English], W. Herz, H. Griesbach and G. W. Kirby, eds., Springer Verlag, Wien **38**, 1979, p. 107.