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biochemical
systematics
and ecology

Biochemical Systematics and Ecology 33 (2005) 952–956

www.elsevier.com/locate/biochemsyseco

Sesquiterpene lactones from *Anthemis wiedemanniana*

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Received 3 November 2004; accepted 23 February 2005

Keywords: Asteraceae; *Anthemis wiedemanniana*; Sesquiterpene lactones; Germacranolides; Eudesmanolide

1. Subject and source

The genus *Anthemis* L., assigned by Bremer (1994) to the tribe Anthemideae (subtribe Anthemidinae) of the Asteraceae, comprises ca. 210 species. The Anthemidinae consist of the genus *Anthemis* with provisional addition of the monotypic genus *Nananthea* DC (Bremer, 1994). *Anthemis wiedemanniana* Fisch. & C.A. Mey. (section Cota) is an endemic species distributed in the Mediterranean, the Middle and the Eastern Anatolian regions of Turkey (Davis, 1975; Strid and Tan, 1999). It is about 10–45 cm high, has a long life and especially occurs on calcareous rocks, step and road

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sides. Aerial parts of *A. wiedemanniana* were collected in Eskisehir, Söğüt near Oluklu Village, step and road sides, 980 m, 23.06.2003, N 40° 04' E 30° 30'. Samples are deposited at the Department of Biology, Çanakkale Onsekiz Mart University with voucher No. Celik 2200-2205. The distribution of this species is shown in Fig. 1.

2. Previous work

Previous chemical studies seem to indicate that sesquiterpene lactone patterns are systematically important within the genus. The presence of sesquiterpene lactones in various *Anthemis* species has been described in ca. 30 papers. The first literature report refers to the bitter sesquiterpene lactone nobilin from *Anthemis nobilis* L., a well known medicinal plant (Benesova et al., 1964). Apart from unusual acyclic lactones isolated from *Anthemis cotula* L. (Bohlmann et al., 1969; Baruah et al., 1985), other *Anthemis* species contain representatives of three major types of sesquiterpene lactones: germacranolides, eudesmanolides and guaianolides (Vajs et al., 1999 and references cited therein; Zaghoul et al., 1989; Vajs et al., 2000; Staneva et al., 2002, 2004; Bruno et al., 2002; Konstantinopoulou et al., 2003). No phytochemical studies on *A. wiedemanniana* have been reported so far.

3. Present study

Air dried and finely powdered aerial parts (900 g) were extracted three times with $(\text{CH}_3)_2\text{CO}$ (5 L) at room temperature for one week. After filtration, the solvent was removed under reduced pressure to yield a residue (31.5 g) which was chromatographed on a silica gel column eluted with pet. ether with increasing amounts of EtOAc; 200 mL fractions being collected as follows: 1–10 (pet. ether), 11–35 (pet. ether–EtOAc, 4:1), 36–61 (pet. ether–EtOAc, 3:2), 62–76 (pet. ether–EtOAc, 2:3), 77–100 (pet. ether–EtOAc, 1:4), 101–117 (EtOAc).

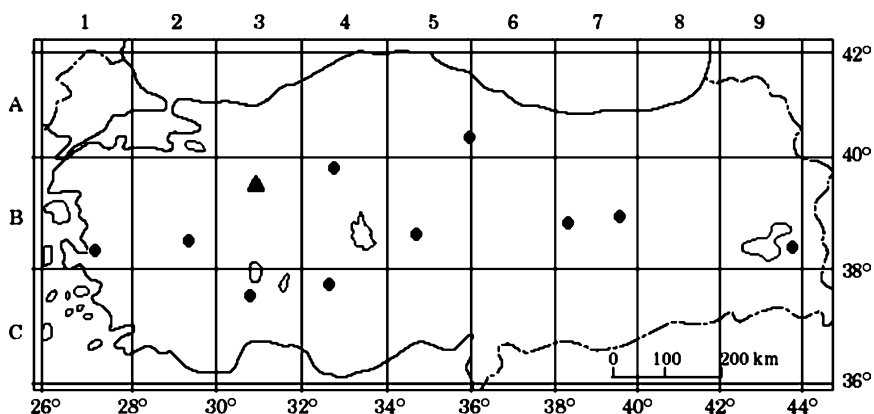
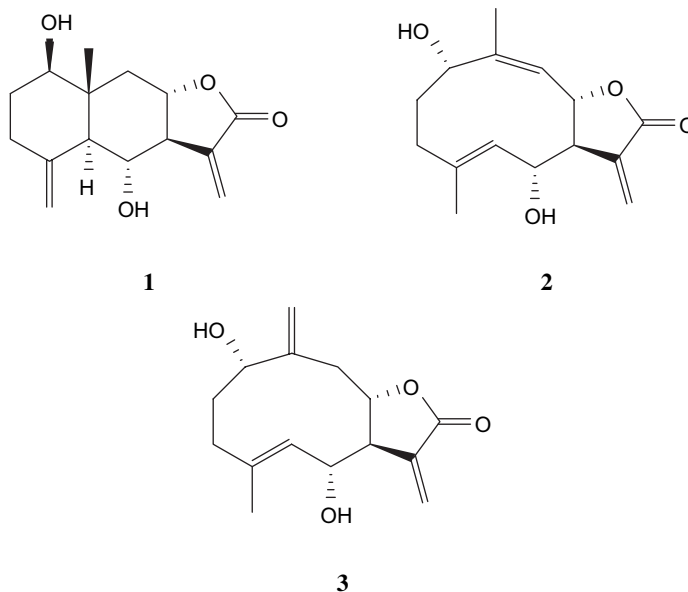


Fig. 1. Distribution of *Artemis wiedemanniana* in Turkey (● area of distribution, ▲ area of collection).

Fractions 77–89 were rechromatographed on a silica gel column, eluting with pet. ether with increasing amounts of EtOAc (3:7 → 7:3) to give three subfractions. The first one was purified by radial chromatography (CH₂Cl₂–MeOH, 19:1) to give 5 mg of deacetyl-β-cyclopyrethrosin (**1**). The second subfraction was purified by radial chromatography (CH₂Cl₂–MeOH, 19:1) to give 15 mg of tatrudin A (**2**). The purification of the third subfraction by column chromatography (pet. ether–EtOAc, 2:3) allowed the isolation of 50 mg of 1-*epi*-tatrudin B (**3**).

Structures of Compounds 1–3



Fractions 90–100 were rechromatographed on a silica gel column, eluting with pet. ether with increasing amounts of EtOAc (3:7 → 7:3) to give further 20 mg of compound **3**.

The structures of the isolated compounds were readily identified by comparing their spectral data with those reported for deacetyl-β-cyclopyrethrosin (**1**) (Bohlmann et al., 1982), tatrudin A (**2**) (Sanz and Marco, 1991) and 1-*epi*-tatrudin B (**3**), also known as tanachin, deacetyldihydrochrysanolide (Sanz and Marco, 1991; Konstantinopoulou et al., 2003) or 1- α -hydroxy-1-deoxotamirin (Rustaiyan et al., 1990). The identity of the structure of tatrudin A (**2**) with deacetylulirinol (Dorskotch et al., 1980) has recently been established (Sanz and Marco, 1991).

4. Chemotaxonomic and ecological significance

Plants of the genus *Anthemis* are represented by 52 taxa in Turkey (Davis, 1975; Davis et al., 1988; Güner et al., 2000). A few of these are important as herbal

medicines and dyes in some regions. *A. wiedemanniana* is a folk remedy for cough and cold. *Anthemis altissima* L. and *A. cotula* L. are used for the treatment of hepatitis (Öztürk and Özçelik, 1991). *Anthemis hyalina* DC. is used as starting material for the production of shampoo and *Anthemis arvensis* L. for activating the urinary system and as sedative (Özel, 1999). Flavonoids of *Anthemis austriaca* Jacq., *A. cotula* L., *Anthemis pseudocotula* Boiss., *Anthemis cretica* L. subsp. *pontica* (Willd.) Grierson, *Anthemis chia* L. and *Anthemis tinctoria* L. var. *tinctoria* are used for yellow coloration of fabric material (Uysal, 1991).

A. wiedemanniana is a very distinct species which appears to be without close relatives. It is similar to *Anthemis pestalozzae* due to its small size and conical receptacles, but differs from this species in the dissection of its leaves (more similar to *A. tinctoria*) and in its unribbed, ecoronate achenes. From a chemotaxonomic point of view it is important to point out that compounds **1–3** have been previously isolated from *A. altissima* (Konstantinopoulou et al., 2003), also a member of the section Cota. This may be indicative of a close relationship between the two species. The antibacterial potential of the three products has been tested in vitro (Konstantinopoulou et al., 2003) and tatrindin A (**2**) has been proven to be active against *Helicobacter pylori*.

Compounds **1–3** seem to be typical secondary metabolites of *Tanacetum* species. For example, compound **1** was reported from *Tanacetum densum* (Lab.) Sch. Bip. subsp. *sivasicum* Hub.-Mor. and Grierson (Gören, 1993), compound **2** was found in *Tanacetum vulgare* L. (Nano et al., 1980; Sanz and Marco, 1991) and *Tanacetum polycephalum* Sch. Bip. (Rustaiyan et al., 1990), and compound **3** was isolated from *T. vulgare* (Sanz and Marco, 1991), *T. polycephalum* (Rustaiyan et al., 1990) and *Tanacetum argenteum* (Lam.) Wild. subsp. *canum* (C. Koch) Grierson var. *canum* (Gören and Tahtasakal, 1997).

The genus *Tanacetum*, placed by Bremer (1994) in the subtribe Tanacetinae, is probably the most problematic genus of the Anthemideae and several of the other subtribes, possibly a large part of the entire tribe, may have their sister groups within *Tanacetum*. The Tanacetinae have most of their representatives in Asia, while the Anthemidinae are mainly distributed in the Mediterranean region (Bremer, 1994).

Acknowledgements

This work was supported by Italian Government project PRIN 2003.

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