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Sesquiterpenoids and phenolics from *Taraxacum hondoense*

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Abstract

Eleven sesquiterpene lactones, including the new guaianolide 11β-hydroxydeacetylmatricarin-8-*O*-β-glucopyranoside, along with four known phenolic glucosides were isolated from *Taraxacum hondoense*. The compounds were characterized by spectral methods.

Keywords: *Taraxacum hondoense*; Sesquiterpenoids; 11β-Hydroxydeacetylmatricarin-8-*O*-β-glucopyranoside; Phenolics

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1. Introduction

Plants of the genus *Taraxacum* (Asteraceae, tribe Lactuceae), including the most popular species *Taraxacum officinale*, have long been used as medicinal herbs. So far, only 10 representatives of this taxon have been investigated chemically [1–3], yielding a number of germacrane-, eudesmane-, and guaiane-type sesquiterpene lactones, along with some other secondary metabolites. The most common sesquiterpene lactone isolated from the plants is the germacranolide taraxinic acid β-glucopyranosyl ester (**1**). The compound, frequently co-occurring with its 11β,13-dihydroderivative (**2**) and the structurally related germacranolide ainslioside (**3**), has been reported from seven species. Recently,

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deacetylmatricarin (**4**) and structurally related 2-oxo-guaianolides with cross-conjugated cyclopentadienone systems, which are more unusual sesquiterpene lactones for this taxon, have been isolated from *Taraxacum platycarpum* [4] and *Taraxacum obovatum* [3]. Compounds of this type are particularly characteristic for plants of the tribe Anthemideae of the Asteraceae, among the better known of which are *Chamomilla recutita* and *Achillea millefolium* aggregate. These non-proazulene guaianolides have been proven to contribute to anti-inflammatory and anti-ulcer activities of the plant extracts [4–7]. The present investigation is concerned with root constituents of *Taraxacum hondoense* Nak. et Koidz., a species originating from Japan, which reportedly contains neolupenyl and tarolupenyl acetates [8].

2. Experimental

2.1. Plant material

The roots of *T. hondoense* were collected in May 2002 from plants growing in the Garden of Medicinal Plants, Institute of Pharmacology, Polish Academy of Sciences, Kraków, where a voucher specimen (01/81) was deposited. Seeds of the plant were obtained from the Medicinal Plant Research Station, National Institute of Health Sciences, Tsukuba, Japan.

2.2. Extraction and isolation

Dried and finely powdered plant material (335 g) was exhaustively extracted with EtOH at room temperature and the solvent was evaporated in vacuo to give a dark brown residue (34 g). The residue was chromatographed on a Si gel (Merck; Art. 7754, 186 g) column, packed in hexane, eluting with a step gradient of hexane–EtOAc (0→50% EtOAc in hexane) followed by EtOAc and finally with 5% and 10% MeOH in EtOAc, all fractions being monitored by TLC. The relevant fractions were combined and further separated by preparative TLC (Merck; Art. 5553) and semipreparative HPLC on a Delta-Pak C-18 column (particle size 15 μm, 25 × 100 mm) coupled to a photodiode array detector using H_2O–MeOH mixtures at a flow rate of 3.0 ml min^{-1}. Elution of the Si gel column with hexane–EtOAc (3:2) afforded crystalline **4** (4.9 mg), after purification by preparative TLC (hexane–EtOAc, 1:1). Combination of fractions eluted with EtOAc, followed by preparative TLC purification ($CHCl_3$–MeOH, 17:3), gave three crude fractions of sesquiterpenoids containing glucosyl moieties. The less polar fraction, after separation by semipreparative HPLC (H_2O–MeOH, 1:1), furnished almost pure **3** (1.1 mg), a mixture of **1** and **2** (ca. 1:1, 12.9 mg), **11** (3.9 mg), **8** (1.2 mg), and a mixture of **9** and **10** (ca. 2.5:1, 1.4 mg), in that order. The medium polar fraction was processed by semipreparative HPLC (H_2O–MeOH, 3:2) to yield **6** (3.8 mg) and additional amounts of **1** (2.0 mg), **2** (1.5 mg), and **11** (2.4 mg). The more polar fraction contained a mixture (13.8 mg) of **5** and **7** as shown by ^1H-NMR. From the mixture, 3.6 mg and 4.4 mg of pure **5** and **7**, respectively, could be separated by semipreparative HPLC (H_2O–MeOH, 7:3). Further elution of the mother column with EtOAc–MeOH (19:1) gave fractions containing