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Secondary metabolites of *Peucedanum tauricum* fruits

Hailemichael Tesso [a,*], Wilfried A. König [a,†], Karl-Heinz Kubeczka [b], Magdalena Bartnik [c], Kazimierz Glowniak [c]

[a] *Institute of Organic Chemistry, University of Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany*
[b] *Institute of Pharmaceutical Biology, University of Würzburg, Julius-von-Sachs-Platz 2, D-97082 Würzburg, Germany*
[c] *Department of Pharmacognosy, Skubiszewski Medical University, 20-093 Lublin, Poland*

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Abstract

From the essential oil of fruits of *Peucedanum tauricum* Bieb., two guaiane type sesquiterpene hydrocarbons guaia-1(10),11-diene (**1**) and guaia-9,11-diene (**2**) were identified. The structures of **1** and **2** were assigned by 1D and 2D NMR analysis. The relative configurations of the compounds were established by 2D-NOESY experiments while the absolute configurations were deduced through chemical correlations with (+)-γ-gurjunene (**9**) and capillary GC analysis using modified cyclodextrins as the stationary phases. From the dichloromethane extract of the less volatile fraction of the fruits, coumarins, viz. peucedanin (**3**), oxypeucedanin hydrate (**4**) and officinalin isobutyrate (**5**) were isolated. Compound **5** was confirmed to be 6-carbomethoxy-7-isobutyroxycoumarin by its 1D and 2D NMR data as well as by conversion into officinalin (**7**) by alkaline hydrolysis. Peuruthenicin, a positional isomer of officinalin, is assigned structure **8** on spectral basis. Bergapten (**6**) was identified by its mass spectrum. This is the first report on the isolation of compounds **4** and **5** from *P. tauricum*.

Keywords: *Peucedanum tauricum* Bieb.; Apiaceae; Essential oil; Guaia-1(10),11-diene; Guaia-9,11-diene; Coumarins; Peucedanin; Officinalin isobutyrate; Oxypeucedanin hydrate; Peuruthenicin; Bergapten

1. Introduction

Peucedanum tauricum Bieb. is an endemic perennial plant of the Apiaceae family, growing in nature at dry hillsides and pinewoods in Crimea, Caucasus, and in Romania (Tutin et al., 1968; Grosgiejm, 1967; Sziszkin, 1955). Previous chemical studies of the plant concerned the identification of phenolic acids in the foliage and fruits (Bartnik et al., 2003), GC/MS analysis of the essential oil of the fruits in which a number of sesquiterpene hydrocarbons were identified (Bartnik et al., 2002), isolation of coumarins from the fruits (Glowniak et al., 2002), isolation of an analog of chlorogenic acid and a chromone from the roots (Baranauskaite, 1970), determination of saponins in roots and fruits (Baranauskaite, 1968) as well as isolation of peucedanin from a combined extract of *P. tauricum* and *P. calcareum* (Baranauskaite and Nikonov, 1965). Here, we report the isolation and structural elucidation of two new guaiane type sesquiterpene hydrocarbons from the essential oil of the fruits of the title plant and isolation of coumarins from the high boiling dichloromethane fraction. In addition, revision of the structures of officinalin isobutyrate, officinalin as well as peuruthenicin is reported.

* Corresponding author. Tel.: +49 40 42838 2831; fax: +49 40 42838 2893.
E-mail address: michaeltesso@yahoo.com (H. Tesso).
† W.A. König passed away on 19th November 2004; his scientific achievements will keep him among us.

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2. Results and discussion

The essential oil obtained from the fruits of *P. tauricum* was analysed by coupled gas chromatography and mass spectrometry (GC/MS). Mass spectra and retention indices of the oil constituents were compared with a library of mass spectra of authentic compounds established under identical experimental conditions (Joulain and König, 1998; Hochmuth et al., 2003). Monoterpene hydrocarbons consisting of tricyclene, myrcene, limonene, (*Z*)-β-ocimene, 2,4(8)-*p*-menthadiene, the oxygenated monoterpene linalool and sesquiterpene hydrocarbons comprising α-ylangene, α-copaen, β-bourbonene, guaia-6,9-diene, selina-5,11-diene, valerena-4,7(11)-diene, γ-amorphene, γ-humulene, α-bulnesene, β-elemene, (*E*)-β-caryophyllene, α-guaiene, α-humulene, and γ-gurjunene were identified. The latter five sesquiterpenes have been earlier identified along with α- and β-selinene and γ-cadinene (Bartnik et al., 2002). Two unknown components were isolated by preparative gas chromatography. Their structures were elucidated by 1D and 2D NMR techniques to be guaia-1(10),11-diene (**1**) and guaia-9,11-diene (**2**), (Fig. 1). The relative configurations of the new compounds were established through 2D NOESY experiments. Their absolute configurations were assigned according to chemical correlations and capillary GC analysis using modified cyclodextrins as stationary phases (König, 1992; König et al., 1999).

In addition, from the less volatile dichloromethane fraction, known coumarins, peucedanin (**3**), oxypeucedanin hydrate (**4**), and officinalin isobutyrate (**5**) were isolated. (Fig. 1). Their structures were established by MS, 1D and 2D NMR data as well as comparison with the literature data (Perel'son et al., 1971; Gonzalez et al., 1976, 1978; Patra and Mitra, 1981; Sun et al., 1982). In addition, the structure of compound **5** was confirmed according to its 1D and 2D NMR data as well as by converting it into officinalin (**7**) by alkaline hydrolysis, thereby clearing the confusion concerning its structure. The earlier reported structure of peuruthenicin (Soine et al., 1973), an isomer of officinalin, is amended to be **8** based on its ^{1}H NMR. Bergapten (**6**) previously reported from the fruits (Glowniak et al., 2002) was identified by its mass spectrum. This is the first report on the isolation of officinalin isobutyrate and oxypeucedanin hydrate from *P. tauricum*.

2.1. Guaia-1(10),11-diene (1)

The mass spectrum of **1** exhibited a molecular ion signal at *m/z* 204 indicating an elemental composition of $C_{15}H_{24}$, typical for a sesquiterpene hydrocarbon with four degrees of unsaturations. The ^{1}H NMR spectrum and 2D HMQC experiment indicated six methylene groups, three methine and three methyl groups confirming the presence of twenty four protons directly attached to carbon atoms. Signals at δ 1.61 (H_3-14) and 1.71 (H_3-

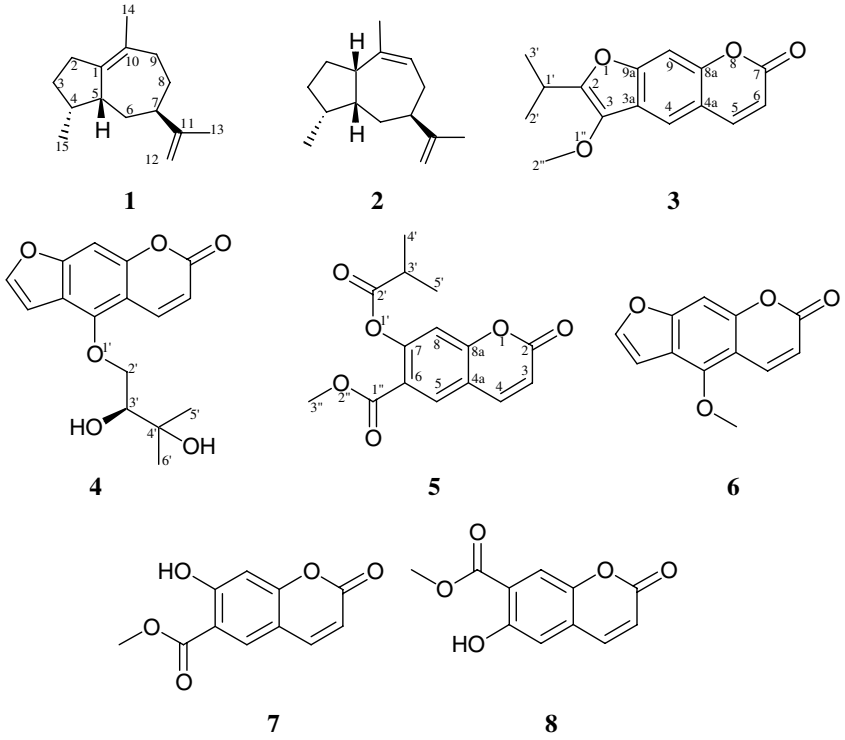

Fig. 1. Selected compounds from *P. tauricum*.