Polish J. Chem., **75**, 1587–1589 (2001) **COMMUNICATION**

Sesquiterpene Lactones from *Taraxacum bicorne*

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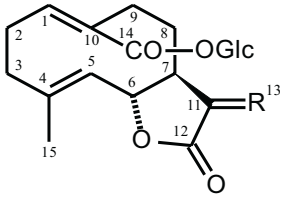
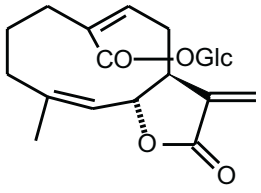
The genus *Taraxacum* belongs to the tribe Lactuceae of the family Asteraceae. Previous phytochemical work on plants of this taxon is limited, with records published for *T. officinale*, the most popular species and a well known traditional herbal remedy [1]. Until now, several other *Taraxacum* species have been investigated yielding a number of germacrane-, eudesmane- and guaiane-type sesquiterpene lactones [2–5], along with some other secondary metabolites. The most common sesquiterpene lactones isolated from the plants are unusual germacranolide acids esterified with glucose (**1** and **2**) and eudesmanolides glucosylated at the C-1 position. The present communication deals with the composition of sesquiterpenoids in roots of *T. bicorne* Dahlst., which has not been examined so far.



1 R = CH_2
2 R = H, αMe



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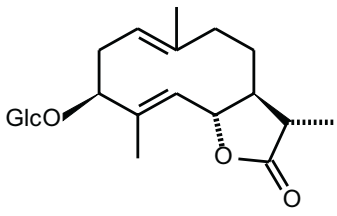

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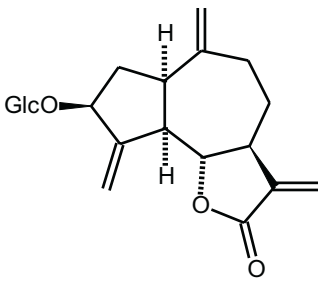

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Glc = β-glucopyranosyl

The fresh roots were extracted with ethanol and the extract was subjected to column and thin layer chromatographies on silica gel to give a crude mixture of compounds **1**–**5**, which showed one major spot on TLC. The compounds required semipreparative RP HPLC for complete resolution. Isolated were, from higher to lower polarity, the following sesquiterpene lactones: ainslioside (**3**, Glc = β-glucopyranosyl) [6], taraxinic acid β-glucopyranosyl ester (**1**) [7], its 11β,13-dihydroderivative (**2**) [7,8], sonchuside A (**4**) [9] and vernoflexuoside (glucozaluzanin C, **5**) [10]. They were readily identified by direct comparison (HPLC, UV – online, ^{1}H NMR) with the compounds previously isolated in our laboratory [8,10,11].

Similarly to some other *Taraxacum* species, the roots of *T. bicorne* contain the germacranolide acid derivatives **1** and **2**, but the above mentioned eudesmanolides could not be detected in the plant material. The hitherto unreported ^{13}C NMR data of **2** are given in Table 1. Since no ^{13}C NMR data in pyridine-d_5 are available for **1**, they are also added to Table 1, in order to facilitate the identification of both compounds in other species. The carbon resonance assignments were supported by HETCOR experiments. The optical rotation value of **2**, not reported previously, is also included in the experimental part. Compound **3**, another germacranolide acid derivative, recently isolated from *T. officinale* in our laboratory [8], was first reported from *Ainsliaea acerifolia* var. *subapoda* (tribe Mutisieae) [6]. The compound co-occurs in *T. officinale* with **1** and **2** [8]. In addition, our study showed the presence of the germacranolide and guaianolide glycosides **4** and **5**, respectively, in the plant roots, the former being the major sesquiterpene lactone. This is the first report on the occurrence of the glycosides **4** and **5** in *Taraxacum* species. The compounds are known as constituents of some other representatives of the tribe Lactuceae [9,11,12].

Plant material: The roots of *Taraxacum bicorne* were collected in August 1998 from plants growing in the Garden of Medicinal Plants of the Institute of Pharmacology, Polish Academy of Sciences in Kraków.

Extraction and isolation: Fresh roots (2.5 kg) were cut into small pieces and submerged in boiling EtOH, and left to stand in a cold room for several days. The solvent was evaporated under reduced preassure providing a residue (157 g) which was prefractionated on a silica gel (Merck, Art. 7733) column using successively hexane, hexane-EtOAc (1:1), EtOAc, EtOAc-MeOH (1:1) and MeOH as eluents to give five fractions of 2 l each. The fractions were concentrated and monitored by TLC. Two fractions eluted with EtOAc and EtOAc-MeOH (1:1) were combined and a residue (20 g) was subjected to column chromatography on silica gel (Merck, Art. 7754) using hexane-EtOAc (up to 100% EtOAc), followed by EtOAc-MeOH (up to 5% MeOH) gradient solvent systems. Fractions from EtOAc elution were further purified by preparative TLC (Merck, Art. 5553, $CHCl_3$-MeOH, 9:1) to afford a crude mixture of **1**–**5** (157.4 mg), a portion (95.3 mg) of which was processed by semipreparative RP HPLC to give **3** (1.3 mg), **1** (16.8 mg), **2** (3.7 mg, $[\alpha]_D^{26}$ –20.7°, c 2.74, MeOH), **4** (26.0 mg) and **5** (1.0 mg), in that order. The separation was performed on a Delta-Pak C-18 column (particle size 15 μm, 25 × 100 mm) coupled to a UV photodiode array detector with MeOH – H_2O (4:6) at a flow rate of 3 ml min^{-1}. Due to some difficulties during

the HPLC separation the isolated amounts do not represent the concentration of pure compounds in the plant material.

Table 1. ^{13}C NMR (125.76 MHz) spectral data[a] of **1** and **2** in pyridine-d_5.

position	**1**, δ_C	**2**, δ_C
1	148.51	148.32
2	26.97	26.90
3	39.36	39.45
4	141.09	141.95
5	126.85	126.99
6	82.16	81.47
7	50.35	54.59
8	30.61	30.65
9	36.78	36.81
10	131.44	131.46
11	143.27	42.46
12	170.52	178.51
13	119.40	13.30
14	166.87	166.85
15	17.14	17.02
Glucosyl carbons		
1	95.77	95.79
2	74.18	74.29
3	78.86	78.87
4	71.27	71.28
5	79.51	79.50
6	62.39	62.39

[a] The chemical shifts were determined from HETCOR correlations.

REFERENCES

1. Blaschek W., Hänsel R., Keller K., Reichling J., Rimpler H. and Schneider G., *Hagers Handbuch der Pharmazeutischen Praxis*, Springer Verlag, Berlin, Heidelberg, NY, Folgeband 3, Drogen L-Z, p.897 (1998).
2. Ho Ch., Choi E.J., Yoo G.S., Kim K.-M. and Ryu S.Y., *Planta Med.*, **64**, 577 (1998).
3. Zidorn C., Ellmerer-Müller E.P. and Stuppner H., *Phytochem.*, **51**, 991 (1999).
4. Zielińska K. and Kisiel W., *Phytochem*., **54**, 791 (2000).
5. Ahmad V.U., Yasmeen S., Ali Z., Khan M. A., Choudhary M.I., Akhtar F., Miana G.A. and Zahid M., *J. Nat. Prod.*, **63**, 1010 (2000).
6. Jin H., *Yakugaku Zasshi*, **102**, 911 (1982).
7. Hänsel R., Kartarahardia M., Huang J.-T. and Bohlmann F., *Phytochem.*, **19**, 857 (1980).
8. Kisiel W. and Barszcz B., *Fitoterapia*, **71**, 269 (2000).
9. Miyase T. and Fukushima S., *Chem. Pharm. Bull.*, **35**, 2869 (1987).
10. Kisiel W., *Polish J. Pharmacol. Pharm.*, **27**, 461 (1975).
11. Kisiel W., Barszcz B. and Szneler E., *Phytochem.*, **45**, 365 (1997).
12. Miyase T., Ueno A., Noro T., Kuroyanagi M. and Fukushima S., *Chem. Pharm. Bull.*, **33**, 4451 (1985).