SESQUITERPENE LACTONES FROM *PICRIS PAUCIFLORA* Willd.

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ABSTRACT

The aerial parts of *Picris pauciflora* Willd. (*Asteraceae*) yielded 11 β , 13-dihydrolactucin, while the roots of the plant afforded 3- β -D-glucopyranosides of 11 β , 13-dihydrozaluzanin C and 9 α -hydroxy-11 β , 13-dihydrozaluzanin C (ixerin F). The guaianolides were isolated from ethanol extracts using chromatographic methods and were identified on the basis of spectral analysis. They are reported for the first time from this species.

KEY WORDS: *Picris pauciflora* Willd., sesquiterpene lactones, guaianolides, glycosides.

INTRODUCTION

In continuation of biochemical systematic studies on sesquiterpene lactones in plants of the tribe *Lactuceae* with distinctive ligulate florets (*Asteraceae* family), the constituents of *Picris pauciflora* Willd. have been investigated.

The genus *Picris* L. consists of some 50 species found in the temperate zone of the northern hemisphere of Eurasia and Mediterranean Basin. Several of the species have already been chemically studied and shown to contain germacrane-, eudesmane-, and guaiane-type sesquiterpene lactones, both free and in glycosidic form (Bohlmann et al. 1981, Nishimura et al. 1986, Bruno and Herz 1988, Hafez et al. 1988, Kanayama and Tada 1988, Kery et al. 1988, Daniewski et al. 1989, Uchiyama et al. 1990, Kijjoo et al. 1992, Kisiel 1992a, 1992b, Marco et al. 1992). The chemistry of the title plant has not been examined so far.

MATERIAL AND METHODS

Whole plants of *P. pauciflora* were collected in the flowering period (August 1990) from the Garden of Medicinal Plants of the Institute of Pharmacology, Polish Academy of Sciences, Kraków, where a voucher specimen was deposited.

Dried and powdered plant material divided into roots (148 g) and aerial parts (1200 g) was separately extracted with ethanol at room temperature and the extracts were concentrated to dryness under reduced pressure.

The root extract (10.5 g) was directly chromatographed on a silica gel column (Merck, Art. 7754) eluting with a hexane-ethyl acetate (9:1 $\rightarrow$ 1:1) gradient solvent system following by

increasing proportions of methanol in chloroform (up to 15%). Elution of the column with chloroform-methanol mixtures (95:5 and 9:1) afforded two crude sesquiterpene lactone glycoside fractions which were purified by preparative TLC (Merck, Art. 5553) using chloroform-methanol (85:15, one or three developments) as a solvent system. The less polar fraction gave 9 mg of **2**, the more polar one yielded 38 mg of **3**. The compounds remained non-crystalline.

The extract from the aerial parts of the plant (72 g) followed by treatment with aqueous lead diacetate and worked up in the usual manner, afforded a residue which was chromatographed on a silica gel column, as described above. Relevant fractions eluted with hexane-ethyl acetate (1:1) were further purified by preparative TLC (chloroform-methanol, 95:5) giving 18 mg of **1**, as colourless crystals (m.p. 91-92°C from methanol). In more polar fractions eluted from the column no sesquiterpene lactone glycosides could be detected.

TABLE 1. ^1H NMR spectral data of 11 β ,13-dihydrolactucin (**1**) (300 MHz, CDCl_3 , TMS as internal standard).

H-3	6.43 d br	H-9'	2.39 dd
H-5	3.75 d br	H-11	2.58 dq
H-6	3.65 t	H-13	1.45 d
H-7	2.13 ddd	H-14	2.44 s br
H-8	3.75 ddd	H-15	4.86 dd
H-9	2.81 dd br	H-15'	4.53 d br
J (Hz): 3,15 = 1.3; 5,6 = 6,7 = 9.8; 7,8 = 10.0; 7,11 = 11.9; 8,9 = 10.8; 8,9' = 2.2; 9,9' = 13.8; 11,13 = 6.9, 15,15' = 17.7.

Fig. 1. The chemical structures of compounds **1-3** (Glc = β -D-glucopyranoside).

RESULTS AND DISCUSSION

The ethanol extracts of the aerial parts and roots of the title plant were repeatedly chromatographed on silica gel to afford the three guaiane-type sesquiterpene lactones **1-3** (Fig. 1).

From the aerial parts 11 β , 13-dihydrolactucin (**1**) was isolated and identified by comparing its melting point and spectral data with those reported (Sarg et al. 1982). Since the reported ^1H NMR data of **1** contain some mistakes, they are given in Table 1.

The roots gave 3- β -D-glucopyranosides of 11 β , 13-dihydrozaluzanin C (**2**) (Zdero and Bohlmann 1987) and 9 α -hydroxy-11 β , 13-dihydrozaluzanin C (**3**) (Asada et al. 1984). The spectral data of the two compounds were identical to those of authentic samples which had been isolated earlier in our laboratory (Kisiel and Kohlmünzer 1987, Kisiel 1992b). The glycoside **3**, known as ixerin F, was found to be the main sesquiterpene lactone constituent of the plant.

The presence of **1-3** in *Picris pauciflora* Willd. links this species to *Picris hieracioides* L. which also synthesizes, among others, the three compounds (Kisiel 1992b, Nishimura et al. 1986).

LITERATURE CITED

- ASADA H., MIYASE T., FUKUSHIMA S., 1984. Sesquiterpene lactones from *Ixeris tamagawaensis* Kitam. II. Chem. Pharm. Bull. 32: 3036-3042.
- BOHLMANN F., ZDERO CH., ROBINSON H., KING R. M., 1981. Sesquiterpene lactones from *Picris echioides*. Phytochemistry 20: 2029-2030.
- BRUNO M., HERZ W., 1988. Eudesmanolides from *Picris aculeata*. Phytochemistry 27: 1201-1203.
- DANIEWSKI W. M., GUMUŁKA M., DROŹDŹ B., GRABARCZYK H., BŁOSZYK E., 1989. Sesquiterpene lactones. XXXVIII. Constituents of *Picris echioides* L. and their antifeedant activity. Acta Soc. Bot. Pol. 58: 351-354.
- HAFEZ S., JAKUPOVIC J., SARG T. M., EL-DOHMIATY M. M., 1988. Sesquiterpene lactone glycoside from *Picris cyanocarpa*. Planta Medica 54: 365.
- KANAYAMA T., TADA M., 1988. Isolation and structural elucidation of two new sesquiterpene lactones, hieracin I and II, from the flowers of *Picris hieracioides* L. var. *japonica*. Bull. Chem. Soc. Jpn. 61: 2971-2972.
- KERY A. M., HUSAIN A., NESZMELY I., 1988. Validity of data from complex screening of sesquiterpene- γ -lactones. Planta Medica 54: 577-578.
- KIJJOA A., VIEIRA L. M. M., CARDOSO J. M., HERZ W., 1992. An eudesmanolide from *Picris spinifera*. Phytochemistry 31: 3635-3636.
- KISIEL W., KOHLMÜNZER S., 1987. Ixerin F from *Crepis biennis*. Planta Medica 53: 390.

- KISIEL W., 1992a. Guaianolides from *Picris altissima*. Phytochemistry 31: 328-329.
- KISIEL W., 1992b. Sesquiterpene lactones from *Picris hieracioides* subsp. *hieracioides*. Planta Medica 58: 115.
- MARCO J. A., SANZ J. F., CARDA M., 1992. Sesquiterpene lactones from *Picris echioides*. Phytochemistry 31: 2163-2164.
- NISHIMURA K., MIYASE T., UENO A., NORO T., KUROYANAGI M., FUKUSHIMA S., 1986. Sesquiterpene lactones from *Picris hieracioides* L. var. *japonica* Regel. Chem. Pharm. Bull. 34: 2518-2521.
- SARG T. M., OMAR A. A., KHAFAGY S. M., GRENZ M., BOHLMANN F., 1982. 11 β , 13-Dihydrolactucin, a sesquiterpene lactone from *Launaea mucronata*. Phytochemistry 21: 1163.
- UCHIYAMA T., NISHIMURA K., MIYASE T., UENO A. 1990. Terpenoid glycosides from *Picris hieracioides*. Phytochemistry 29: 2947-2951.
- ZDERO CH., BOHLMANN F., 1987. Sesquiterpene lactones from the genus *Brachylaena*. Phytochemistry 26: 2579-2601.

LAKTONY SESKWITERPENOWE *PICRIS PAUCIFLORA*

STRESZCZENIE

W etanolowych wyciągach z *Picris pauciflora* Willd. (*Asteraceae*) stwierdzono, po raz pierwszy w tym gatunku, występowanie laktonów seskwiterpenowych typu gwajanu. Metodami chromatograficznymi wyodrębniono z nadziemnych części rośliny 11 β , 13-dihydrolaktucynę, a z korzeni – 3- β -D-glukopiranozydy 11 β , 13-dihydrozalużaniny C i 9 α -hydroksy-11 β , 13-dihydrozalużaniny C (ikseryna F). Związki te zidentyfikowano na podstawie analizy spektralnej.

SŁOWA KLUCZOWE: *Picris pauciflora* Willd., laktony seskwiterpenowe, gwajanolidy, glikozydy.