

Sesquiterpene lactones and monoterpene glucosides from plant species *Picris echioides*

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Investigation of the constituents of the aerial parts of domestic plant species *Picris echioides* afforded the sesquiterpene lactones, *i.e.*, guaianolides jacquilenin (**1**), 11-*epi*-jacquilenin (**2**), achillin (**3**) and eudesmanolide telekin (**4**). The chemical identification of the two monoterpene glucosides (–)-*cis*-chrysanthemol-β-D-glucopyranoside (**5**) and its 6'-acetate **6** is also reported. The guaianolide achillin (**3**) and the two monoterpene glucosides **5** and **6** were isolated for the first time from this plant species. Isolation was achieved by column chromatography and the structures were established mainly by the interpretation of their physical and spectral data, which were in agreement with those in the literature.

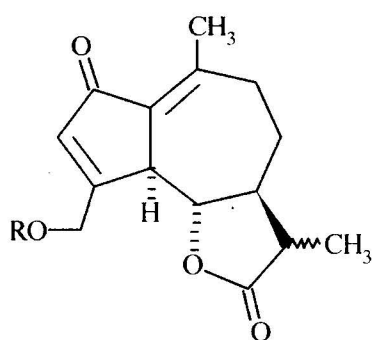
Keywords: *Picris echioides*, *Lactuceae*, sesquiterpene lactones, monoterpene glucosides.

INTRODUCTION

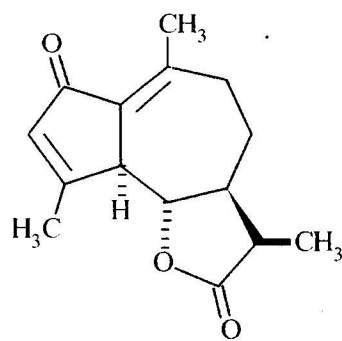
The small genus *Helminthia* from the tribe *Lactuceae* (family *Asteraceae*), comprising 6 species is a native floral element, as the widespread weed of the central Europe and Mediterranean region. In Serbia only one species grows (*H. echioides*), which has extensive name as syn. *Picris echioides* L.¹ This species can be found throughout the world, *i.e.*, southern Asia and also in the North America, where it is a major weed problem. As far as traditional medicine is concerned, *Picris echioides* has been used as alcoholic extract for the treatment of indigestion and against intestinal nematodes and other parasites.¹

As a result of the numerous biological activities, secondary metabolites of the members of this genus have received considerable attention.² As far as the biological activity is concerned, among the most interesting compounds isolated from these species are: sesquiterpene lactones, flavonoids and terpenoid glycosides (mainly in the aerial parts).^{3–6} Hitherto, several sesquiterpenes and sesquiterpene lactones, almost

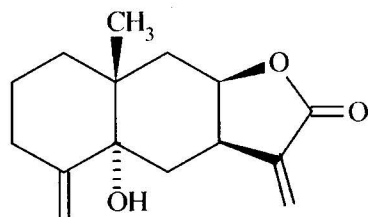
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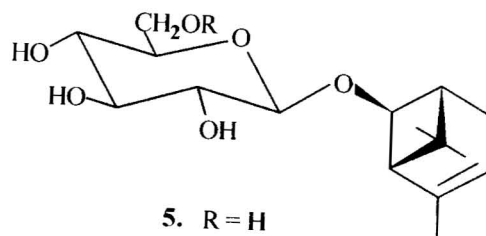
1. R = H, 11 β H
1a. R = Ac, 11 β H
2. R = H, 11 α H
2a. R = Ac, 11 α H



3.



4.



- 5. R = H
- 6. R = Ac

The results obtained from this investigation assigned the lactucin-like sesquiterpenes (C(15)-OH guaian) may be the characteristic at least for some groups of the tribe *Lactuceae*. Furthermore, the presence of 11,13-dihydro compounds seems to be typical. So, the chemical picture of the domestic plant species of *Picris echooides*, which can be drawn from these results, is expected from the chemotaxonomic point of view of this tribe.⁸ Monoterpene glucosides are not usual in the genus either.

EXPERIMENTAL

Plant material

Aerial parts of *Picris echooides* L. has traditional name Grgusa (family *Asteraceae*, tribe *Lactuceae*)^{1,19} were collected in the vicinity of Mt. Rudnik in July 1995 and 1996 and authenticated by Dr. P. Marin, from the Department of Botany at the Faculty of Biology, University of Belgrade. A voucher specimen has been deposited in the herbarium of this Department.

Extraction and isolation

Air-dried, finely ground aerial parts of *P. echooides* (2.5 kg) were extracted for 48 h at room temperature with petrol-Et₂O-MeOH, 1:1:1 (10 liters). After concentration at reduced pressure in a rotary evaporator, the residue was dissolved in boiling MeOH (1 liter) and cooled to the room temperature. The supernatant liquid was decanted from the waxy precipitate and then concentrated *in vacuo*, giving 32 g of dark greenish oil as residue. This residue was prefractionated by column chromatography on silica gel. The three fractions were collected after elution with solvents: petrol-Et₂O, 1:3, **A**; Et₂O, **B** and finally with Et₂O-MeOH, 6:1, fraction **C**. The fractions **A**, **B** and **C** were subjected for further repeated CC on silica gel, respectively.

Fraction **A** (18 g) contained mainly the pigments, waxes and wide spread sterols. Elution was begun with petrol-Et₂O, 9:1 and then gradually increasing the polarity by addition of Et₂O, giving the lactone **3** with petrol-Et₂O (8 mg, recrystallised from hexane-ether). It was isolated as colorless needles, melted at 133–134 °C and $[\alpha]_D = +115$ (c, 1, CHCl₃), same as the literature,¹⁴ EIMS, *m/z* (rel. int. %): 246 (M⁺, 47), 231 (6), 217 (23), 203 (25), 190 (15), 91 (100) and the other spectral data corresponded to those published. The polar fraction **B** (5.2 g), contained the material eluted with Et₂O, previously, was further submitted to CC, starting with petrol-Et₂O (1:1). The two main fractions were selected after the inspection by NMR and in the next step fractionated by HPLC (RP-18, MeOH-H₂O, 3:2, *ca* 150 bar), respectively. The first fraction could not be separated by HPLC containing mixture of the epimers **1** and **2**. Acetylation (Ac₂O, 2 h, 70 °C) it gave the acetates, which were separated by silica gel CC, with petrol-Et₂O (2:1) affording the **1a**, with $[\alpha]_D = +105$ ° (c, 0.7, CHCl₃) (12 mg) and **2a**, with $[\alpha]_D = +44$ ° (c, 0.1 CHCl₃) (8 mg), as colorless gummy materials. Their IR, NMR and MS data corresponded to those published. The second fraction, after separation by HPLC yielded lactone telekin (**4**, 13 mg), as the white crystals.

The more polar fraction **C** (2.5 g) was separated by silica gel CC (Et₂O-MeOH, 7:1) yielding the (–)-*cis*-chrysanthenol-β-D-glucopyranoside (**5**, 18 mg), gum with $[\alpha]_D = -44$ ° (c, 0.8, MeOH); IR (ν_{\max} cm⁻¹): 3400, 1368, 1210, 1070, 1040, 1025, 760. EIMS *m/z* (rel. int.): 296.1624 (M-H₂O)⁺ (8), 268 (4), 192 (8), 190 (20), 175 (16), 149 (22), 134 (33), 119 (82), 93 (59), 91 (100), 55 (67). Calc. for C₁₆H₂₆O₆-H₂O, M⁺, 296.1618. The compound **5** (10 mg) was dissolved in 10 ml of methanol and 20 ml of 6 % HCl was added. The solution was heated on a water bath for 45 min, cooled and extracted several times with water. The solvent was removed *in vacuo* and the remaining substance identified as (–)-*cis*-chrysanthenol and glucose was also detected in the water solution.¹⁶ Elution with Et₂O-MeOH, 7:1 as solvent mixture also afforded (–)-*cis*-chrysanthenol-β-D-glucopyranoside-6'-acetate (**6**, 11 mg), gum with $[\alpha]_D = -126$ ° (c, 0.5, MeOH); IR (ν_{\max} cm⁻¹): 3400, 1725, 1436, 1365, 1250, 1215, 1080, 1030, 750. EIMS *m/z* (rel. int.): 296.1624 (M-HOAc)⁺ (20), 192 (38), 190 (29), 175 (42), 149 (90), 134 (38), 119 (100), 107 (48), 105 (31), 93 (55), 91 (80). Calc. for

C₁₈H₂₈O₇-HOAc, M⁺, 296.1618. NMR ¹³C- and ¹H- spectral data corresponded to those published.¹⁸

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ИЗВОД

СЕСКВИТЕРПЕНСКИ ЛАКТОНИ И МОНОТЕРПЕНСКИ ГЛУКОЗИДИ БИЉНЕ ВРСТЕ

Picris echoides L.

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Из надземног дела домаће биљне врсте *Picris echoides* (фамилија *Asteraceae*), корова познатог под именом Гргуша, изолована су и идентификована четири сесквитерпенса лактона, као и два монотерпенса глукозида. Идентификовани лактони су гвајанолиди јаквиленин (**1**), 11-*epi*-јаквиленин (**2**) и ахилин (**3**) као и еудесманолителекин (**4**). Монотерпенси глукозиди (–)-*cis*-кризантенол-*b*-*D*-глукопиранозид (**5**) и његов 6'-ацетат, **6** су такође изоловани из истог екстракта. Гвајанолид ахилин (**3**) и монотерпенси глукозиди (**5,6**) су по први пут изоловани из ове биљне врсте, док су преостала три лактона изолована више пута из европске биљне врсте.

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