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A SESQUITERPENE LACTONE GLYCOSIDE FROM *CREPIS TECTORUM*

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Key Word Index—*Crepis tectorum*; Compositae; sesquiterpene lactone; guaianolide glucoside; tectoroside.

Abstract—Tectoroside, the minor constituent of *Crepis tectorum*, was isolated and characterized as 3-(4-hydroxyphenyl)lactate of 8-epidesacylcynaropicrin glucoside.

INTRODUCTION

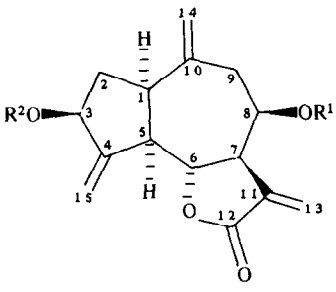
In the course of a search for sesquiterpene lactones from the genus *Crepis* (tribe Lactuceae, Compositae) we have examined the roots of *Crepis tectorum* L. and isolated a series of known guaianolide-type sesquiterpene glycosides [1]. The presence of an unidentified minor constituent in this series has also been announced [1].

A repeat study with somewhat larger amounts of the plant material and careful chromatography of the polar fractions have allowed the isolation of a new ester of 8-epidesacylcynaropicrin glucoside, named tectoroside (**1**). The structure and relative stereochemistry of the compound were deduced on the basis of some chemical transformations and spectroscopic studies.

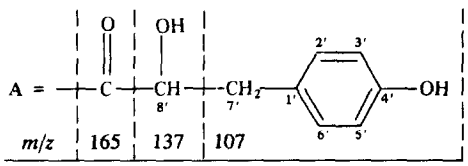
RESULTS AND DISCUSSION

Tectoroside (**1**) was difficult to purify and it could not be induced to crystallize. As its ^{1}H NMR spectrum was not clear, the enzymatic and alkaline hydrolytic products furnished indirect evidence for its structure.

Alkaline hydrolysis of **1** afforded 8-epidesacylcynaropicrin glucoside (**2**) identified by direct comparison with an authentic sample. The glucoside isolated for the first time from *Crepis capillaris* (L.) Wallr. [2], was also found in the title species [1].



	R^1	R^2
1	A	Glc
2	H	Glc
3	A	H
4	$A(Ac)_2$	Ac



Hydrolysis of **1** with β-glucosidase yielded an aglycone (**3**) and glucose as a sugar. The mass spectrum of **3** exhibited a molecular ion at *m/z* 426 which corresponded with the proposed molecular formula $C_{24}H_{26}O_7$. Further prominent peaks at *m/z* 408 and 226 indicated the loss of water and the acid ($C_9H_{10}O_4$), respectively.

Acetylation of **3** gave a triacetate **4** whose ^{1}H NMR spectrum allowed assignment of the structure of **3**. In the spectrum three sharp three-proton singlets were observed corresponding to aromatic (δ2.28) and aliphatic (δ2.12 and 2.03) acetates. The signals of the sesquiterpene part were nearly identical with those of 8-epidesacylcynaropicrin esters [3–5]. The remaining signals indicated the presence of a 3-(4-hydroxyphenyl)-lactyl diacetate residue. The A_2B_2 type doublets (both $J = 8$ Hz) at δ7.23 and 7.02 were accounted for two pairs of aromatic protons. The signals at δ3.03 ($J = 14$, 8.5 and 5 Hz) and 5.12 ($J = 8.5$ and 5 Hz) were assigned to benzylic protons and the proton geminal to an acetoxyl group, respectively. The chemical shifts and couplings of the protons corresponded to those of (*R*)-3-aryllactates [6].

These data were corroborated by diagnostic mass spectral peaks. In the mass spectrum of **3** the peaks of ions formulated as $CH_2{=}C_6H_4{=}\overset{+}{O}H$ and $HO{-}C_6H_4{-}CH_2{-}CH{=}\overset{+}{O}H$ were observed at *m/z* 107 (100%) and 137, respectively, as anticipated. Moreover, the prominent peaks at *m/z* 164 and 147 in the mass spectra of **3** and **4** were attributed to the ions probably formed by elimination of water or acetic acid and ketene from $[RCO_2H]^+$ and $[RCO]^+$, respectively.

Thus, the structure of tectoroside (**1**) was established as 8-epidesacylcynaropicrin-8-*O*-[3-(4-hydroxyphenyl)-lactyl]-3-*O*-β-D-glucopyranoside. To the best of our knowledge sesquiterpene lactones esterified with aryllactic acids have not been detected previously.

EXPERIMENTAL

Plant material. The roots of *Crepis tectorum* were collected in August, 1987, from the medicinal plant garden of the Institute of Pharmacology, Polish Academy of Sciences, in Kraków where a specimen sample was preserved.

Extraction and isolation. The dried and powdered plant material (310 g) was extracted with EtOH at room temp. until the extract was colourless. The residue (13 g), after removal of the

Table 1. ^{1}H NMR spectral data of compound **4** (300 MHz, $CDCl_3$, TMS as int. standard)

H		H	
1	2.93 *br q*	14b	4.92 *s*
2a	2.44 *dt*	15a	5.54 *t*
2b	1.79 *dt*	15b	5.33 *t*
3	5.56 *m**	2′	7.23 *d*
5	2.82 *br t*	6′	
6	4.41 *t*	3′	7.02 *d*
7	3.14 *ddd*	5′	
8	5.53 *m**	7a′	3.03 *dq*
9a	2.58 *dd*	7b′	
9b	2.33 *dd*	8′	5.12 *dd*
13a	6.31 *d*	OAc	2.28 *s*
13b	5.47 *d*		2.12 *s*
14a	5.07 *s*		2.03 *s*

*Signals partially overlapped

J(Hz): 1,2a = 8; 1,2b = 7; 2a,2b = 14; 2a,3 = 8; 2b,3 = 7; 1,5 = 5,6 = 6,7 = 9.5; 3,15 = 5,15 = 2; 7,13a = 3.5; 7,13b = 3; 7,8 = 2.5; 8,9a = 8,9b = 6; 9a,9b = 14; 2′,3′ = 5′,6′ = 8; 7a′,7b′ = 14; 7a′,8′ = 5; 7b′,8′ = 8.5

solvent, was chromatographed on a silica gel (70–230 mesh, Merck) column to furnish fractions containing impure **1** on elution with $CHCl_3$–MeOH (9:1). The compound was purified by repeated chromatography using $CHCl_3$–MeOH gradient solvent system; 9 mg of gummy **1** was obtained.

Alkaline hydrolysis of **1**. The compound (3 mg) was treated with aq. 2% NaOH (2 ml) for 1.5 hr at room temp. The mixture was acidified with dil. HCl and extracted with EtOAc to give compound **2** identified by direct comparison with an authentic sample (co-TLC, IR, MS).

Enzymatic hydrolysis of **1**. To the aq. acetate buffer soln (pH 5) of **1** (5 mg) β-glucosidase was added, and the mixture kept at 37°. After reaction was completed, the mixture was extracted with EtOAc. Purification of the crude product by chromatography on silica gel ($CHCl_3$–MeOH, 97:3) afforded **3**. Colourless gum; MS 15 eV, *m/z* (rel. int.): 426 $[M]^+$ (0.7), 408 $[M-H_2O]^+$ (6.9), 390 $[M-2\times H_2O]^+$ (0.5), 333 (0.8), 302 (1.8), 284 (0.4), 244 $[M-RCO_2H]^+$ (1.4), 226 $[M-RCO_2H-H_2O]^+$ (4.1), 182 $[RCO_2H]^+$ (1.4), 181 $[RCO_2]^+$ (0.8), 164 $[RCO_2H-H_2O]^+$ (4.0), 147 $[RCO-H_2O]^+$ (3.8), 137 (0.9), 136 (2.3), 119 (1.1), 107 (100). The water layer was analysed together with different standard sugars on a cellulose TLC plate developed in pyridine–EtOAc–HOAc–H_2O (36:36:7:21). Glucose was detected.

Acetylation of **3**. Compound **3** (2 mg) treated with Ac_2O–pyridine in the usual way gave **4**. Colourless solid; MS 15 eV, *m/z* (rel. int.): 552 $[M]^+$ (2.6), 510 $[M-C_2H_2O]^+$ (51), 492 $[M-HOAc]^+$ (3.0), 450 $[M-HOAc-C_2H_2O]^+$ (57), 390 $[M-2\times HOAc-C_2H_2O]^+$ (100), 244 $[M-RCO_2H-C_2H_2O]^+$ (5.0), 226 $[M-RCO_2H-HOAc]^+$ (43), 206 $[RCO_2H-HOAc]^+$ (5.5), 164 $[RCO_2H-HOAc-C_2H_2O]^+$ (19), 147 $[RCO-HOAc-C_2H_2O]^+$ (43), 98 (7.3), 79 (7.5); ^{1}H NMR: see Table 1.

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