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GUAIANOLIDES FROM *TAECKHOLMIA* SPECIES

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Key Word Index—*Taeckholmia pinnata*; *T. microcarpa*; *T. arborea*; *T. capillaris*; Compositae; sesquiterpene lactones; guaianolides.

Abstract—The investigation of four *Taeckholmia* species afforded in addition to known desacylcynaropicrin, two new guaianolides. The structures were elucidated by spectroscopic methods and chemical transformations. The chemotaxonomy is discussed briefly.

INTRODUCTION

So far investigations of representatives of genus *Sonchus* have shown that guaianolides related to jacquinelin may be characteristic of this genus [1, 2; González, A. G., unpublished results]. We have now studied the sesquiterpene lactones of four species of the genus *Taeckholmia*, which has been segregated from *Sonchus* [3].

In addition to desacylcynaropicrin, two new sesquiterpene lactones were isolated, all related to desacylcynaropicrin. These lactones seem to be of chemotaxonomic importance.

RESULTS AND DISCUSSION

The aerial parts of *Taeckholmia pinnata* afforded a complex mixture of three sesquiterpene lactones, which were separated by repeated TLC. Their structures were deduced from ^{1}H NMR spectra and chemical transformations. The major compound was the desacylcynaropicrin (1), the structure of which was determined by comparison of its physical and spectroscopic properties with those of an authentic sample. The minor compounds were the new desacylcynaropicrin derivatives 2 and 3.

10α-Hydroxy-10,14-dihydrodesacylcynaropicrin (2) was a crystalline product, mp 105–108°. The mass spectrum indicated a molecular ion at m/z 280 in agreement with the molecular formula $C_{15}H_{20}O_5$. The IR spectrum showed the presence of an α,β-unsaturated-γ-lactone moiety (1760 cm^{-1}) and hydroxyls (3360 and 1040 cm^{-1}), one of them tertiary, which resisted acetylation with acetic anhydride in pyridine at room temperature. The ^{1}H NMR spectrum (Table 1) was very similar to that of desacylcynaropicrin. The major difference in the spectrum of 2 was the absence of the C-14 exomethylene protons and the appearance of a singlet at δ1.22 assigned to a methyl group attached to a carbon bearing a hydroxyl group.

Acetylation of 2 with acetic anhydride and pyridine gave a crystalline diacetate **2a**, mp 185–86°, which was treated with thionyl chloride in pyridine to give a mixture of acetate isomers **1a** (^{1}H NMR: δ4.94 *br s* and 5.32, H-14) and 4 (^{1}H NMR: δ5.5 H-9 and 1.80 *br s* C-10–Me). Dehydration indicated that the tertiary hydroxyl at C-10 was *cis* to H-1 and α.

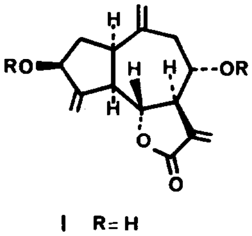
10-α-Hydroxy-8-desoxy-10,14-dihydrodesacylcynaropicrin (3), was obtained as an oil. The mass spectrum clearly gave the molecular formula $C_{15}H_{20}O_4$ with fragments at m/z 246 $[M-H_2O]^+$ and 228 $[M-2H_2O]^+$. The ^{1}H NMR spectral data (Table 1) were very similar to those of 2 except for the upfield shift of the signal of H-8.

Lactone 3 gave the monoacetate **3a** on acetylation with acetic anhydride-pyridine. The IR spectrum indicated the presence of a hydroxyl group, and in the ^{1}H NMR spectrum the singlet at δ5.26 shifted downfield to 5.40.

These results have some chemotaxonomic relevance, because they indicate that the investigated *Taeckholmia* species are chemically uniform and distinct from the investigated *Sonchus* species [4].

EXPERIMENTAL

Mps are uncorr. ^{1}H NMR spectra were recorded at 60 MHz using TMS as internal standard. Analytical TLC was performed



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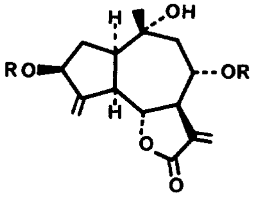
1a R = Ac



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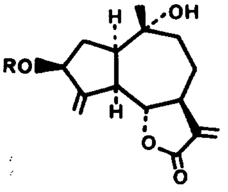

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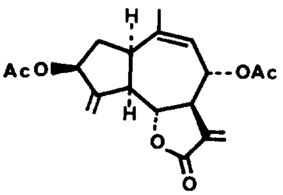

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Table 1. ^{1}H NMR spectral data for compounds **1**–**3a** (60 MHz, TMS as internal standard)

	1	**1a**	**2**	**2a**	**3**	**3a**
H-1	2.55 *m*		2.6 *m*		2.2 *m*	
H-2a H-2b	1.7–2 *m*		1.6–1.9 *m*		1.90 *m*	
H-3	4.4 *m*		4.4 *m*		4.50 *br s*	
H-6	4.10 *t* (10)*		4.08 *t* (10)		4.23 *t* (10)	
H-8	3.75 *t* (6)		4.1 *t* (6)		—	
H-9a H-9b	2.2 *m*		2.2 *m*		2.3 *m*	
H-13a	6.13 *br s*		6.12 *d* (3)		6.14 *d* (3)	
H-13b			5.98 *d* (3)		5.42 *d* (3)	
H-14a H-14b	5.03 *br s*		1.23 *s*		1.20 *s*	
H-15a H-15b	5.25 *br s*		5.32 *br s*		5.26 *br s*	
OAc		2.07 *s* 2.13 *s*		2.05 *s* 2.17 *s*		2.05 *s*

*Figures in parentheses are coupling constants in Hertz.

on silica gel and CC was on silica gel. The plant material was extracted with EtOH.

Taekholmia pinnata (L.fil) Boulos (voucher TFC 18331). The aerial parts (2.300 kg), collected in Tegueste (Tenerife) afforded 200 mg **1** (C_6H_6–EtOAc 1:1), 20 mg **2** (EtOAc) and 30 mg **3** (EtOAc).

Taeckholmia microcarpa Boulos (voucher TFC 18328). The aerial parts (3.100 kg) collected in Güimar (Tenerife) afforded 840 mg **1**, 300 mg **2** and 400 mg **3**.

Taeckholmia arborea (DC) Boulos (voucher TFC 18329). The aerial parts (500 g) grown from seeds from the ICONA Garden (Tenerife), afforded 40 mg **1**, 60 mg **2** and 50 mg **3**.

Taeckholmia capillaris (Svent) Boulos (voucher TFC 18330). The aerial parts (3.200 kg) collected in Masca (Tenerife) afforded 1.2 g **1**, 500 mg and 500 mg **3**.

10α-Hydroxy-10,14-dihydrodesacylcynaropicrin (**2**). Colourless crystals, mp 105–108° (EtOAc–*n*-hexane). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3480–3360 (OH), 1760 (γ-lactone); MS *m/z* (rel. int.): 262.1227 $[M-H_2O]^+$ (2.91) ($C_{15}H_{18}O_4$), 244 $[M-2H_2O]^+$ (4.20), 228 $[M-3H_2O]^+$ (3.49).

Acetate **2a** was prepared by acetylation of **2** (100 mg) with Ac_2O–pyridine to provide 80 mg of the acetate **2a** after CC purification (C_6H_6–CH_3COCH_3 8:2), mp 185–86°. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 3580 (OH), 1750 (γ-lactone), 1727, 1240 (OAc); MS *m/z* (rel. int.): 364 $[M]^+$ (1), 322 $[M-C_2H_2O]^+$ (4) ($C_{17}H_{22}O_6$).

Dehydration of **2a**. Compound **2a** (80 mg) was dissolved in pyridine (1 ml) and $SOCl_2$ (0.5 ml) was added at 0°. The resulting soln was left 1 hr. The reactant was treated in the usual manner to give a crude oil which showed two spots on TLC. The presence of a mixture of the acetate isomers **1a** (^{1}H NMR: δ4.94 *br s* and 5.32, H-14) and **4** (^{1}H NMR: δ5.5, H-9 and 1.80 *br s*, C-10–Me) can be deduced from its spectroscopic study.

10α-Hydroxy-8-desoxy-10,14-dihydrodesacylcynaropicrin (**3**). Colourless gum. IR $\nu_{\max}^{\mathrm{CHCl_4}}$ cm^{-1}: 3580 (OH), 1750 (γ-lactone); MS *m/z* (rel. int.): 246.1272 $[M-H_2O]^+$ (11.2) ($C_{15}H_{18}O_3$), 228 $[M-2H_2O]^+$ (17.6).

Acetate **3a**. Acetylation of **3** (20 mg) with Ac_2O–pyridine at room temp. overnight gave, after the usual work up, 18 mg of the monoacetate **3a** which remained non-crystalline. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 3590 (OH), 1753 (γ-lactone), 1725 (OAc). MS *m/z*: 306 $[M]^+$ ($C_{17}H_{22}O_5$), 264 $[M-COCH_2]^+$, 246 $[264-COCH_2]^+$, 228 $[246-H_2O]^+$.

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