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UROSPERMAL, A GLUCOSIDE FROM *UROSPERMUM PICROIDES*

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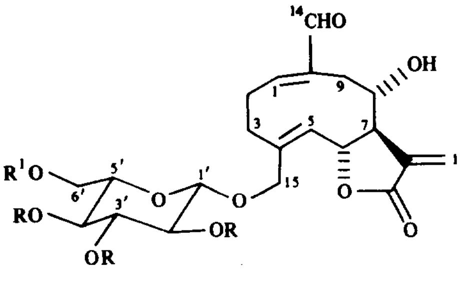
Key Word Index—*Urospermum picroides*; Compositae; sesquiterpene lactones; urospermal A glucoside.

Abstract—The roots of *Urospermum picroides* afforded urospermal A 15-*O*-*β*-D-glucoside.

The aerial parts of *Urospermum picroides* (L.) Scop. ex F. W. Schmidt contain the melampolide urospermal A and the *p*-hydroxyphenyl acetate of the corresponding glucoside [1]. We have now studied the polar fractions from the roots. Thin-layer chromatography afforded two compounds, the glucosides **1** and **2**. Acetylation gave the acetates **3** and **4**, the latter being identical with the acetylation product of the glucoside **2** isolated from the aerial parts [1]. The ^{1}H NMR spectrum of **3** (Table 1) was close to that of **4**. However, the signals of the *p*-hydroxyphenyl acetate were replaced by an additional acetate methyl signal. As observed previously [1] the hydrogen-bonded 8α-hydroxyl group was not acetylated. The ^{1}H NMR spectrum of the natural compound **1** could be measured only in deutero-pyridine (Table 1). All signals were assigned by spin decoupling in the usual way, starting with the H-7 signal although all signals were



1 R = R^1 = H
2 R = H, R^1 = $COCH_2C_6H_4OH$ (p)
3 R = R^1 = Ac
4 R = Ac, R^1 = $COCH_2C_6H_4OAc$ (p)

Table 1. ^{1}H NMR spectral data of compounds **1** and **3** (400 MHz, TMS as internal standard)

	1 (C_5D_5N)	**3** ($CDCl_3$)
H-1	6.67 *br dd*	6.81 *br dd*
H-2	2.53 *ddd*	2.54 *m*
H-2′	2.26 *ddd*	
H-3	2.68 *ddd*	2.61 *ddd*
H-3′	1.80 *br dd*	2.03 *m*
H-4	5.15 *br d*	5.15 *br d*
H-6	4.98 *dd*	4.57 *dd*
H-7	2.65 *dddd*	2.45 *dddd*
H-8	4.27 *ddd*	3.90 *dddd*
H-9	2.98 *dd*	2.70 *dd*
H-9′	2.44 *br d*	2.37 *br d*
H-13	6.60 *dd*	6.52 *dd*
H-13′	6.33 *dd*	6.30 *dd*
H-14	9.49 *br s*	9.44 *br s*
H-15	4.77 *d*	4.40 *d*
H-15′	4.44 *d*	4.33 *d*
H-1′	4.91 *d*	4.58 *d*
H-2′	4.00 *dd*	5.04 *dd*
H-3′	4.20 *m*	5.22 *dd*
H-4′		5.08 *dd*
H-5′	3.95 *m*	3.73 *dd*
H-6′$_1$	4.54 *dd*	4.26 *dd*
H-6′$_2$	4.36 *dd*	4.17 *dd*
OH	6.06 *d*	6.07 *d*
OAc	—	2.08 *s* 2.03 *s* 2.02 *s* 1.98 *s*

J (Hz): 1, 2 = 9; 1, 2′ = 8; 1, 9 ~ 1; 5, 6 = 6, 7 = 7, 8 = 10; 7, 13 = 3.5; 7, 13′ = 3; 8, OH = 11, 5; 8, 9 = 5; 8, 9′ = 11; 9, 9′ = 16; 13, 13′ = 2; 15, 15′ = 12; 1′, 2′ = 8.5; 2′, 3′ = 3′, 4′ = 4′$_1$, 5′ = 9.5; 5′, 6′$_1$ = 2.5; 5′, 6′$_2$ = 5; 6′$_1$, 6′$_2$ = 12.

broadened and some were partly overlapped. The ^1H NMR spectrum of **3** in deutero-chloroform was very clear and again all the signals were assigned by spin decoupling. The presence of a β-glucoside moiety followed from the couplings. While electron impact mass spectrometry gave no molecular ions, the chemical ionization mass spectra of **1** and **3** gave clear $[M+1]^+$ ions.

EXPERIMENTAL

The fresh roots (2 kg, voucher No. UP 83) were cut and extracted with MeOH, the extract was concd under red. pres. and extracted with EtOAc. The extract (6.3 g) was separated by CC (silica gel) eluted with $CHCl_3$–MeOH (19:1). Two fractions containing the major compounds were purified by TLC ($CHCl_3$–EtOH, 4:1, silica gel G 254). The less polar constituent (R_f 0.49) gave colourless crystals (145 mg), mp 112–115° and acetylation (Ac_2O, 2 hr, 70°) afforded **4**, identical with an authentic sample (400 MHz ^1H NMR and TLC). The more polar fraction (**1**) (R_f 0.24) was crystallized from $CHCl_3$–MeOH, mp 124–126° (180 mg). IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3400 (OH), 1760 (γ-lactone), 1665 (C=CCHO); MS (CI, *i*-butane) *m/z* (rel. int.): 441 $[M+1]^+$ (11), 423 $[441-H_2O]^+$ (3), 391 $[423-MeOH]^+$ (20), 279 $[\text{aglycone}+1]^+$ (66), 261 $[279-H_2O]^+$ (93), 243 $[261-H_2O]^+$ (100). Acetylation (Ac_2O, 2 hr, 70°) afforded **3**, colourless crystals from MeOH, mp 169–171°. IR $\nu_{\max}^{\mathrm{CHCl_3}}$ cm^{-1}: 3400 (OH), 1750 (γ-lactone, OAc), 2750, 1675, 1610 (C=CCHO); MS (CI, *i*-butane) *m/z* (rel. int.): 609 $[M+1]^+$ (0.5), 591 $[609-H_2O]^+$ (4), 331 (100), 271 $[331-HOAc]^+$ (24), 211 $[271-HOAc]^+$ (9), 169 $[211-\text{ketene}]^+$ (48).

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TRITERPENES FROM *PERIANDRA DULCIS* ROOTS

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Key Word Index—*Periandra dulcis*; Leguminosae; triterpenes; roots; 3,25-dioxoolean-12(13)-en-30-oic acid; 3,25-dioxoolean-18(19)-en-30-oic acid.

Abstract—Two new triterpenes from the root of *Periandra dulcis* were found to be 3,25-dioxoolean-12(13)-en-30-oic acid and 3,25-dioxoolean-18(19)-en-30-oic acid.

INTRODUCTION

Triterpene glycosides, periandrin I, II, III and IV have already been reported as sweet components from water extract of the roots of *Periandra dulcis* Mart. [1–3]. In this paper, the isolation of two new triterpenes from the same plant material and the confirmation of their structures is described.

RESULTS

The mixture of triterpenes from the ethyl acetate extract of the roots of *Periandra dulcis* was dissolved in petrol and separated by chromatography on a silica gel column with *n*-hexane–acetone (5:1).

Compound **1** was crystallized from acetone–water as colourless needles, mp 290–296°, with the elemental composition, $C_{30}H_{44}O_4$ estimated by high resolution mass spectrometry. In the IR spectrum carbonyl absorptions appeared at 1730 and 1685 cm^{-1}. The ^1H NMR spectrum showed six singlet methyl protons between δ 0.82–1.20, an olefinic proton at 5.26 as a multiplet and a formyl proton at 10.45 as a singlet. Compound **1a**, derived from compound **1** by esterification with diazomethane, $C_{31}H_{46}O_4$, mp 234–237°, gave a singlet for the carbomethoxy protons at δ 3.70 besides the proton signals shown for compound **1** in the ^1H NMR spectrum. The mass spectra of compounds **1** and **1a** showed retro-Diels–Alder fragments of the C-ring at *m/z* 248, 203 [248 − COOH], 262 and 203 [262 − COOMe], respectively, corresponding to fragments of periandric acid II [1].

Compound **2** crystallized as colourless needles from acetone–water, mp 283–292°, and was formulated as $C_{30}H_{44}O_4$ by its high resolution mass spectrum. Carbonyl group absorption appeared at 1700 cm^{-1} in the IR spectrum and six singlet methyl protons, and olefinic proton and a formyl proton were seen at δ 0.80–1.30, 5.20 and 10.40, respectively, in the ^1H NMR spectrum. The mass spectrum of compound **2** showed characteristic fragments at *m/z* 248, 234, 219, 189 [234 − COOH] and