broadened and some were partly overlapped. The ^{1}H 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 ^{1}H NMR and TLC). The more polar fraction (**1**) (R_f 0.24) was crystallized from $CHCl_3$–MeOH, mp 124–126° (180 mg). IR ν_{max}^{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 [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 $\nu_{max}^{CHCl_3}$ 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 $[211-ketene]^+$ (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

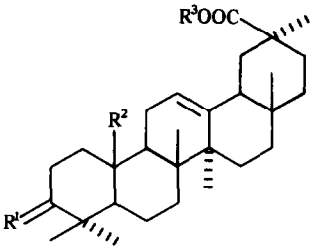
Triterpene glycosides, periandrin I, II, III and IV have already been reported as sweet components from water extract of the roots of *Periandra dulcis* Mart. [1–3]. In this paper, the isolation of two new triterpenes from the same plant material and the confirmation of their structures is described.

RESULTS

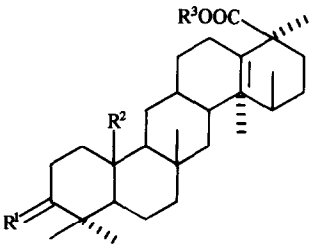
The mixture of triterpenes from the ethyl acetate extract of the roots of *Periandra dulcis* was dissolved in petrol and separated by chromatography on a silica gel column with *n*-hexane–acetone (5:1).

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 ^{1}H 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 ^{1}H 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 ^{1}H NMR spectrum. The mass spectrum of compound **2** showed characteristic fragments at *m/z* 248, 234, 219, 189 [234 − COOH] and



	R^1	R^2	R^3
1	O	CHO	H
1a	O	CHO	Me
1b	H,OH (β)	CHO	H
1c	H,OAc (β)	CHO	Me
1d	H,OH (β)	CH_2OH	H



	R^1	R^2	R^3
2	O	CHO	H
2a	O	CHO	Me
2b	H,OH (β)	CHO	H
2c	H,OAc (β)	CHO	Me
2d	H,OH (β)	CH_2OH	H

188 [248 − COOH] consistent with corresponding peaks in the spectra of $\Delta^{18(19)}$-oleane derivatives such as periandric acids I and III [2, 3]. Its methyl ester **2a**, mp 210°, gave a carbomethoxy signal at δ 3.67 in the ^{1}H NMR spectrum.

On the bases of the above mentioned spectroscopic data, compounds **1** and **2** were assumed to be olean-12(13)-ene and olean-18(19)-ene triterpenes, respectively, with a ketone, carboxy and formyl group. Thus, reduction of **1** and **2** with sodium borohydride gave the mono- (**1b** and **2b**) and di-alcohols (**1d** and **2d**), which were identical (mmp, IR and ^{1}H NMR spectra) with authentic periandric acids II, I, IV and III, respectively [1–3]. Methylation followed by acetylation of the monoalcohols **1b** and **2b** gave the monoacetyl methyl esters **1c** and **2c**, identical in every respect with the monoacetyl methyl esters of periandric acids II and I, respectively.

Consequently, compounds **1** and **2** were identified as 3,25-dioxoolean-12(13)-en-30-oic acid and 3,25-dioxo-olean-18(19)-en-30-oic acid.

EXPERIMENTAL

Extraction and separation. The chipped and dried roots of *P. dulcis* (4 kg) were refluxed × 3 with EtOAc (7 l.) for 5 hr. The extracts were combined, concd *in vacuo* and dissolved in petrol (3 × 4 l.). The combined filtrates were concd and chromatographed on a silica gel column eluting with *n*-hexane–Me_2CO (5:1) to give compounds **1** and **2**, which were detected by spraying with 10% H_2SO_4 and heating on TLC.

Compound **1**. Mp 290–296°; $[\alpha]_D^{25}$ + 123.68° ($CHCl_3$, *c* 0.642); IR ν_{max}^{KBr} cm^{-1}: 3200 (COOH), 1730 (C=O), 1685 (COOH); ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.82, 0.98, 1.00, 1.16, 1.18, 1.20 (3H each, *s*, 6 × Me), 5.26 (1H, *m*, H-12), 10.45 (1H, *s*, CHO); MS: *m/z* 468.321 (M^+, calc. for $C_{30}H_{44}O_4$, 468.324), 439 [M − 29 − 15]$^+$, 248, 219, 230.

Compound **2**. Mp 283–292°; $[\alpha]_D^{23}$ + 1.52° ($CHCl_3$; *c* 1.275); IR ν_{max}^{KBr} cm^{-1}: 3150 (COOH), 1700 (C=O); ^{1}H NMR (60 MHz, $CDCl_3$): δ 0.80 (3H, *s*, Me), 1.06 (6H, *s*, 2 × Me), 1.13, 1.27, 1.30 (3H, each *s*, 3 × Me), 5.20 (1H, *s*, H-19), 10.40 (1H, *s*, CHO); MS *m/z*: 468.328 (M^+, calc. for $C_{30}H_{44}O_4$, 468.324), 439 [M − 29]$^+$, 248, 234, 219, 207, 189 (100%), 188.

Methylation of compound **1**. Compound **1** (105 mg) in $CHCl_3$ (30 ml) was methylated with CH_2N_2 to give the methyl ester (32 mg) crystallized from Me_2CO–H_2O. Mp 234–237° (colourless needles); IR ν_{max}^{KBr} cm^{-1}: 1730 (COOMe), 1700 (C=O); ^{1}H NMR: δ 0.80, 0.99, 1.02 (3H each, *s*, 3 × Me), 1.16 (6H, *s*, 2 × Me), 1.19 (3H, *s*, Me), 3.70 (3H, *s*, COOMe), 5.25 (H, *t*-like, H-12), 10.43 (1H, *s*, CHO); MS *m/z*: 482.238 (M^+, calc. for $C_{31}H_{46}O_4$, 482.337), 453 [M − 29]$^+$, 354 (100%), 423 [M − 59]$^+$, 262, 203.

Hydrogenation of compound **1**. Compound **1** (22 mg) in *i*-PrOH (20 ml) was stirred with $NaBH_4$ (60 mg) at room temp. for 42 hr. The reaction mixture was neutralized with 2 N HCl, evapd and diluted with H_2O (20 ml). The products were extracted with $CHCl_3$, washed, evapd and separated by chromatography on a silica gel column with *n*-hexane–Me_2CO (5:1). The first eluted compound was identical with perandric acid II and the second with periandric acid IV.

Methylation and acetylation of compound **1b**. Compound **1b** (2.1 mg) in $CHCl_3$ was treated with CH_2N_2 as mentioned above followed by acetylation as usual. The product was crystallized from Me_2CO–H_2O, mp 300°, which was consistent with periandric acid II monoacetyl methyl ester.

Methylation and hydrogenation of compound **2**. These reactions were done in the same manner as described for compound **1**.

Methyl ester (**2a**). Mp 210°; IR ν_{max}^{KBr} cm^{-1}: 1730 (COOMe), 1710 (C=O); ^{1}H NMR: δ 0.79 (3H, *s*, Me), 1.04 (9H, *s*, 3 × Me), 1.13 (3H, *s*, Me), 1.25 (3H, *s*, Me), 3.67 (3H, *s*, COOMe), 5.16 (1H, *s*, H-19), 10.40 (1H, *s*, CHO); MS *m/z*: 482.339 (M^+, calc. for $C_{31}H_{46}O_4$, 482.340), 423 [M − 59]$^+$, 230, 189.

Mono-(**2b**) *and di-* (**2d**) *alcohols.* These were produced by treatment of **2** with $NaBH_4$ and were identical with periandric acid I and III, respectively.

Monoacetyl methyl ester (**2c**). This was given by treatment of compound **2b** with CH_2N_2 and Ac_2O and was identified as the monoacetyl methyl ester of periandric acid I.

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