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TRITERPENES FROM *PERIANDRA DULCIS* ROOTS

YOHEI HASHIMOTO, HIROYUKI ISHIZONE, MIDORI MORIYASU, KAZUKO KAWANISHI, ATSUSHI KATO and MASARU OGURA*

Kobe Women's College of Pharmacy, Higashinada-ku, Kobe, 658, Japan; *Research Laboratory, Yamasa Shoyu Co. Ltd., Chosi, Chiba, 288, Japan

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Key Word Index—*Periandra dulcis*; Leguminoseae; triterpenes; periandric acid I and II, 3-oxo-25-hydroxy-olean-12(13)-en-30-oic acid.

Abstract—Three oleanane triterpenes were isolated from the roots of *Periandra dulcis*, and identified as 3β-hydroxy-25-al-olean-18-en-30-oic acid (periandric acid I), 3β-hydroxy-25-al-olean-12-en-30-oic acid (periandric acid II) and 3-oxo-25-hydroxy-olean-12-en-30-oic acid. The former two compounds (periandric acids I and II) were identical with the aglycones obtained by hydrolysis of periandrin I and II, respectively, and the latter one was a new triterpene.

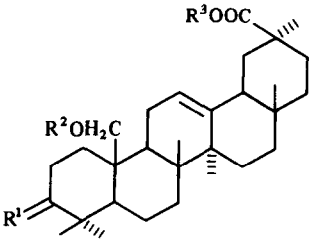
INTRODUCTION

3,25-Dioxoolean-12-en-30-oic acid and 3,25-dioxoolean-18-en-30-oic acid [1] have been isolated from the ethyl acetate extract of the roots of *Periandra dulcis*. This paper describes the isolation and identification of three more triterpenes from the same extract.

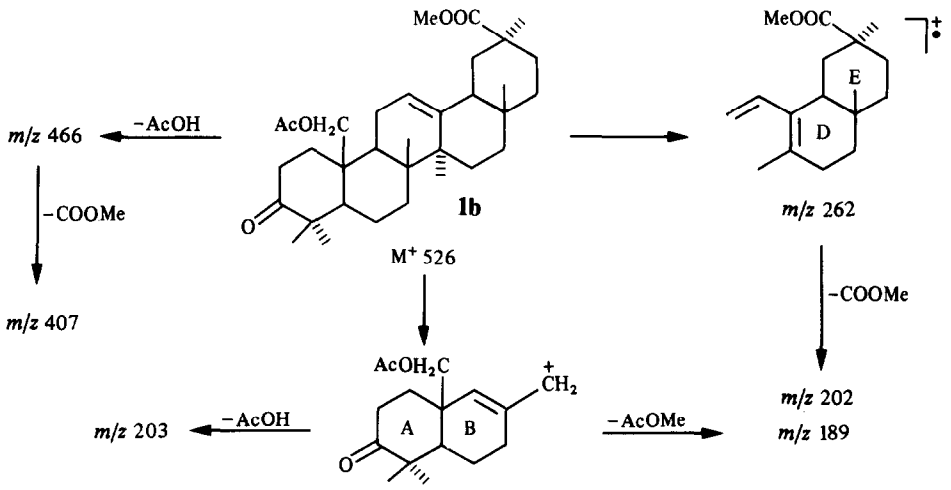
RESULTS

3,25-Dioxoolean-12-en-30-oic acid and 3,25-dioxoolean-18-en-30-oic acid [1] were eluted from a silica gel column with *n*-hexane–acetone (5:1), followed in turn by two further compounds which were crystallized from acetone–water as colourless needles, mp 247–255° and 268–273°, respectively. These later compounds were assumed to be periandric acid II [2] and I [3], by comparison of their R_fs on TLC and mps with those of the authentic samples derived from periandrin II [2] and I [3], respectively. Their identifications were confirmed by comparison of the methyl esters and the monoacetyl methyl esters of the compounds with those of the authentic compounds, by means of undepressed mixture mp, IR and ^{1}H NMR spectra.

Compound **1**, which eluted fifth from the silica gel column with *n*-hexane–acetone (5:1) was crystallized from acetone–water as colourless needles, mp 260–263°; $[\alpha]_D^{23°}$ +183.36 (*c* 0.625, $CHCl_3$), $C_{30}H_{46}O_4$ estimated by high resolution mass spectrometry. The IR spectrum of compound **1** showed the presence of hydroxyl (at ν 3400 cm^{-1}) and carbonyl (at ν 1710 cm^{-1}) groups. By treatment with diazomethane, compound **1** gave a monomethyl ester, mp 213–214°, $C_{31}H_{48}O_4$. The ^{1}H NMR spectrum of the methyl ester (**1a**) showed six singlet methyl protons between δ0.76–1.12, carbomethoxy protons at δ3.68 (singlet), hydroxy methyl protons at δ3.95 and 4.26 (doublet, J = 10 Hz) and an olefinic proton at δ5.33 (*t*-like). Acetylation of **1a** produced an acetyl methyl ester (**1b**), mp 91–103° (colourless powder), $C_{33}H_{50}O_5$. In the ^{1}H NMR spectrum of **1b** the acetyl methyl group appeared at δ1.98 and the protons of the acetyl bearing methylene were shifted to δ4.32 as a singlet. The mass spectrum of **1b** exhibited significant peaks at m/z 262 and 202 [262 − COOMe]$^+$, which could be assigned to fragments consisting of the D and E rings derived by retro-Diels–Alder cleavage and m/z 203 and 189 which could be unequivocally assigned to fragments of A and B rings by a cleavage of the C ring and elimination of AcOH and AcOMe, respectively (Scheme 1). On the basis of the spectroscopic evidence for compound **1**, and its derivatives (**1a** and **1b**) compound **1** was assumed to be an olean-12-ene triterpene containing ketone, carboxyl and hydroxymethyl groups. Compound **1** was hydrogenated with sodium borohydride to give a diol (**1c**), mp > 300°, which was followed by methylation with diazomethane to obtain a methyl ester (**1d**), mp 225–227°. The compounds **1c** and **1d** were identified as periandric acid IV and its monomethyl ester respectively, by means of mmp, IR and ^{1}H NMR. Therefore, compound **1** was determined to be 3-oxo-25-hydroxy-olean-12-en-30-oic acid.



	R^1	R^2	R^3
1	O	H	H
1a	O	H	Me
1b	O	Ac	Me
1c	H(α) OH(β)	H	H
1d	H(α) OH(β)	H	Me



Scheme 1. Mass spectral fragmentation of compound **1b**.

EXPERIMENTAL

Extraction and separation. Compounds in the EtOAc extract [1] were eluted with *n*-hexane–Me_2CO (5:1) from a silica gel column. Compounds were detected by TLC with spraying with 10% H_2SO_4 and heating. Periandric acid II, mp 247–255° (colourless needles from Me_2CO–H_2O). Methyl ester mp 214–217°. Acetyl methyl ester mp > 300°. Periandric acid I, mp 268–273° (colourless needles from Me_2CO–H_2O). Methyl ester mp 197–199°. Acetyl methyl ester mp > 300°. Compound **1** mp 260–263° (colourless needles from Me_2CO–H_2O), $[\alpha]_D^{23°}$, +183.36 (*c* 0.625, $CHCl_3$) IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1710 (C=O), MS *m/z*: 470.339 $[M]^+$ (calc. for $C_{30}H_{46}O_4$, 470.338), 425 $[M-45]^+$, 409, 285, 248, 203, 119 (base peak).

Methylation of compound **1**. Compound **1** (38 mg) in $CHCl_3$ (10 ml) was methylated with CH_2N_2 to give methyl ester (**1a**, 19 mg), crystallized from Me_2CO–H_2O, mp 213–214° (colourless needles); IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1710 (COOMe, C=O), ^1H NMR (60 MHz, $CDCl_3$): δ0.76, 0.90, 0.98, 1.03 (3H, each, *s*, 4 × Me), 1.12 (6H, *s*, 2 × Me), 3.68 (3H, *s*, COOMe), 3.95 and 4.26 (2H, AB type, J = 10 Hz, 25-H_2), 5.33 (1H, *br s*, H-12), MS *m/z*: 484.352 $[M]^+$ (calc. for $C_{31}H_{48}O_4$, 484.349), 425 $[M-59]^+$, 299, 262, 241, 211, 203, 193, 119 (base peak).

Acetylation of compound **1a**. Compound **1a** was acetylated with Ac_2O–pyridine to give **1b**, mp 91–103° (colourless powder); IR ν_{max}^{KBr} cm^{-1}: 1730 (COOMe, OAc, C=O); ^1H NMR: δ0.80, 0.97, 1.02, 1.04, 1.12, 1.18 (3H, each, *s*, 6 × Me), 1.98 (3H, *s*, COOMe), 3.80 (3H, *s*, OAc), 4.32 (2H, *s*, 25-H_2), 5.30 (1H, *m*, H-12), MS *m/z*: 526.367 $[M]^+$ (calc. for $C_{33}H_{50}O_5$, 526.369), 466 $[M-60]^+$, 407 $[M-60-59]^+$, 301, 262, 202, 189, 55 (base peak).

Hydrogenation of periandric acid II. Periandric acid II (28.5 mg) in *iso*-PrOH (10 ml) was stirred with $NaBH_4$ (60 mg) at 80° for 1 hr. The reaction mixture was neutralized with 2 N HCl, evaporated, extracted with $CHCl_3$, dried, evaporated and crystallized from Me_2CO–H_2O. The crystalline compound (mp > 300°) was confirmed as periandric acid IV by means of mmp.

Methylation of compound **1c**. Compound **1c** (14 mg) in $CHCl_3$ (10 ml) was methylated with CH_2N_2 to give a methyl ester (**1d**, 7 mg), which was confirmed to be the methyl ester of periandric acid IV by means of mmp and IR.

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