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MINOR TRITERPENES FROM *ORTHOPTERYGIUM HUANCUY*

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Abstract—Two new triterpenes, 3-oxo-20-hydroxy-lupan-28-oic and 3β,6β-dihydroxy-olean-18-en-28-oic acids, along with oleanonic, morolic and sumaresinolic acids have been isolated from *Orthopterygium huancuy*. The structure of the first new terpene was determined by single crystal X-ray analysis.

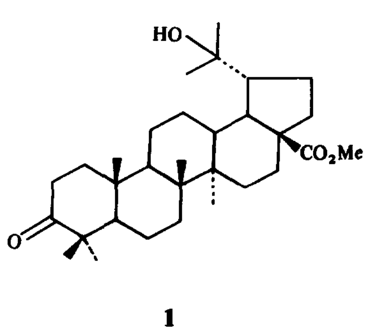
INTRODUCTION

In a previous paper [1], we reported the isolation of 3-oxo-6β-hydroxy-olean-18-en-28-oic, betulonic, moronic and 3-oxo-6β-hydroxy-olean-12-en-28-oic acids from *Orthopterygium huancuy* (Gray) Hemsl (Julianaceae). We report here on the isolation from the same plant of the new triterpenes, 3-oxo-20-hydroxy-lupan-28-oic and 3β,6β-dihydroxy-olean-18-en-28-oic acids, and the known ones oleanonic [2], morolic [3] and sumaresinolic acids [4].

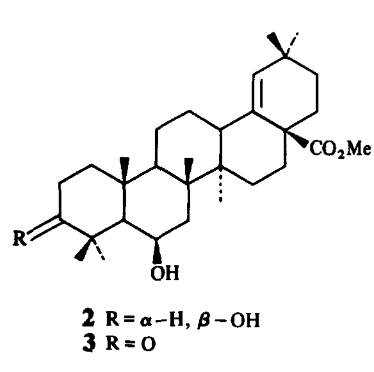
RESULTS AND DISCUSSION

All of the compounds isolated in this study were minor components and were isolated in methyl ester form, by previous treatment of some fractions of the main chromatography with diazomethane. The known compounds were characterized by their physical and spectroscopic constants.

The more polar of the new compounds had a mass spectrum in accordance with a triterpenic acid methyl ester with two hydroxyl groups. In its ^{1}H NMR spectrum the geminal protons to this last function appeared at δ 3.46 and 4.83, as a triplet and a broad singlet respectively. In addition, the chemical shift and the resonance form, δ 5.15 (*s*), of the vinylic hydrogen were typical of an olean-18-ene skeleton with an esterified acid at C-28 [5]. This data suggested that the compound was the methyl ester of 3β, 6β-dihydroxy-olean-18-en-oic acid (**2**). Support for this was provided by the finding that the new compound was



1



2 R = α-H, β-OH
3 R = O

identical with the $3\beta,6\beta$-dihydroxy compound obtained together with the 3α-epimer by reduction of the methyl ester of 3-oxo-6β-hydroxy-olean-18-en-28-oic acid (**3**) with sodium borohydride [1].

The other new compound exhibited hydroxyl absorption as well as absorption for two carbonyl groups in the IR spectrum. Its ^{1}H NMR spectrum showed resonances for seven methyl groups, but not for vinylic protons or hydrogens geminal to an alcoholic function. Therefore the alcohol group had to be tertiary. As this compound was isolated in minute quantities and several structures were in accord with the above data, an X-ray structural analysis was undertaken. In this way the structure 3-oxo-20-hydroxy-lupan-28-oic acid was determined in the form of its methyl ester (**1**).

Compound **1**, $C_{31}H_{50}O_4$, crystallized in the monoclinic system, space group 12. A cell of $a = 23.299(2)$, $b = 6.727(1)$, $c = 17.758(2)$ Å and $\beta = 91.55(1)°$ was chosen, with $Z = 4$ and $\rho = 1.162$ g cm^{-3}. The intensities of the 1719 Friedel pairs up to $\theta = 55°$ were collected in the $\omega/2\theta$ scan mode on an automatic diffractometer with graphite-monochromated CuKα radiation. The crystal structure was solved by MULTAN [6], and least square refined using the 925 observed reflexions with $1 > 3\sigma$ (1). H-atoms were located at their expected positions (methyls disordered) excepting the hydroxyl H-atom, which was found in a difference map. Including the H-atom contribution, a weighting scheme to normalize $\langle wF \rangle$ vs $\langle Fo \rangle$ and $\langle \sin\theta/\lambda \rangle$ was carried out. A final weighted anisotropic full-matrix refinement (fixed isotropic contribution for H-atoms) converged to $R = 7.6\%$ and $R_w = 8.9\%$ [7]. Both hkl and $\overline{hkl}$ reflexions were included in this refinement, omitting 25 pairs affected by secondary extinction. Figure 1 shows the X-ray molecular model with the absolute configuration determined for a similar molecule by X-ray diffraction [8]. The rings B, C and D are almost chairs, ring A is a twist and the five membered ring E is in the C_2 conformation.

In a similar X-ray determined triterpenoid molecular model [9] with C-3 saturated, ring A was changed to a chair, ring B was modified slightly, and rings C, D and E were unchanged. There was a long intermolecular H-bond O_4H . . . . O_1 of 2.89(1) Å.

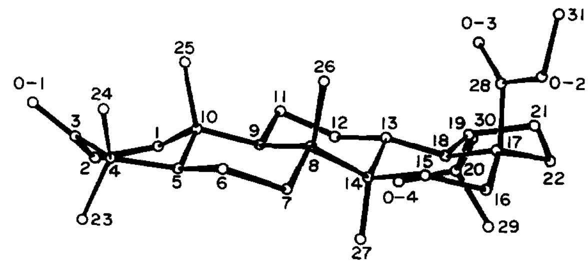


Fig. 1 Stereoscopic view of compound **1**.

EXPERIMENTAL

Mps: uncorr; optical activities and IR. $CHCl_3$; NMR (90 MHz). $CDCl_3$; MS: 70 eV (probe).

Isolation of the products. The extraction and chromatography have been reported previously [1]. The compounds here described were isolated by rechromatography on a dry column of the mixtures of the more polar substances obtained in the last fractions eluted with petrol–EtOAc (9:1).

Oleanonic acid methyl ester (55 mg), mp 182–184° (from $CHCl_3$–MeOH), $[\alpha]_D + 74$ (lit. [2] mp 181–182°, $[\alpha]_D + 76$), $[M]^+$ at m/z 468.3597 (Calc. for $C_{31}H_{48}O_3$ 468.3603). IR ν_{max} cm^{-1}: 3005, 2940, 2860, 1720, 1705, 1455, 1430, 1380, 1260, 1160; ^{1}H NMR: δ0.78, 0.90 and 0 92 (each 3H, *s*), 1.06 (6H, *s*), 1.08 and 1 16 (each 3H, *s*), 2.38 (2H, *m*), 2.87 (2H, *m*), 2.97 (2H, *m*), 3.64 (3H, *s*), 5.32 (1H, *t*); MS m/z: 468 $[M]^+$, 453, 419, 407, 262, 249, 203 (100%), 189.

Morolic acid methyl ester (30 mg), mp 230–233° (from MeOH), $[\alpha]_D + 28$ (lit. [3] mp 228–229°, $[\alpha]_D + 26$) IR ν_{max} cm^{-1}: 3600, 1705, 1445, 1365, 1200, 1030; ^{1}H NMR: δ0.75 (6H, *s*), 0.85 (3H, *s*), 0.94 (12H, *s*), 3.15 (1H, *t*), 3.66 (3H, *s*), 5.14 (1H, *s*); MS m/z: 470 $[M]^+$, 455, 411, 393, 262, 249, 203, 189 (100%).

3-Oxo-20-hydroxy-lupan-28-oic acid methyl ester (**1**) (25 mg), mp 191–193° (from MeOH) $[M-H_2O]^+$ at m/z 468.3638 (Calc for $C_{31}H_{48}O_3$ 468.3604). IR ν_{max} cm^{-1}: 3420, 2910, 1720, 1685, 1450, 1380, 1365, 1155, 1120; ^{1}H NMR: δ0.97 (6H, *s*), 1.04, 1.06, 1 10, 1.15 and 1.27 (each 3H, *s*), 2.35 (4H, *m*), 3.72 (3H, *s*); MS m/z: 468 $[M-H_2O]^+$, 453, 428, 408, 393, 369, 262, 249, 233, 205, 203, 189 (100%).

Sumaresinolic acid methyl ester (30 mg), mp 223° (from MeOH), $[\alpha]_D + 52$ (lit. [4] mp 222–223°, $[\alpha]_D + 53$). IR ν_{max} cm^{-1}: 3550, 3470, 2955, 1710, 1460, 1430, 1260, 1170, 1070, 1030, 1020, 820; ^{1}H NMR: δ0 90, 0.93, 1.02, 1.05, 1.11, 1.18 and 1 29 (each 3H, *s*), 2.90 (1H, *q*), 3.14 (1H, *t*), 3 62 (3H, *s*), 4.54 (1H, *s*, *br*), 5.29 (1H, *m*); MS m/z: 486 $[M]^+$, 468, 453, 450, 435, 426, 302, 262, 249, 203 (100%), 189, 187, 133.

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