

3-OXO-28,29-DIHYDROXYOLEAN-12-ENE FROM
ORTHOSPHENIA MEXICANA

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In previous work, we described the structural determination of orthosphenic acid and netzahualcoyone from *Orthosphenia mexicana* Standley (Celastraceae) (1,2). Continuing with the chemical examination of this species, we describe here the isolation of a new triperpene, 3-oxo-28,29-dihydroxyolean-12-ene (**1**) from the aerial parts.

Structure **1** was assigned to the new triterpene on the basis of the following consideration: its molecular formula, determined by hrms, was $C_{30}H_{48}O_3$. The ir spectrum showed bands of hydroxyl and carbonyl groups. The 1H -nmr spectrum showed signals of a vinylic proton, two hydroxymethylenes, and six tertiary methyl groups. The chemical shift of the hydrogen of the double bond was characteristic of an amirinic triterpene. The ms of this compound also revealed the typical *retro*-Diels Alder fragmentation of ring C of olean-12-ene derivatives (3) with a peak at 250 (334 *m/z* for the diacetate **2**). These data indicated that the two hydroxyl groups are at

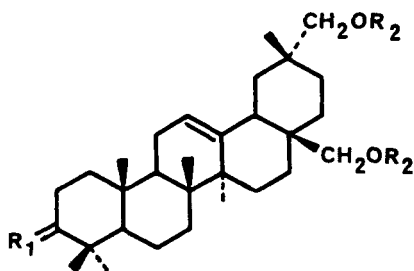
either carbons 28, 29, or 30. This compound did not form an acetonide by treatment with $Me_2CO-CuSO_4$; therefore, one of the alcoholic groups must be at C-28 and the other at C-29 or C-30. Acetylation of **1** formed the diacetate **2**.

Reduction of **1** with $LiAlH_4$ and acetylation afforded a triacetate **3**, different from queratarol triacetate ($3\beta,28,30$ -trihydroxyolean-12-ene triacetate) (**4**) obtained by reduction and acetylation of serjanic acid (**5**) (4). The new triterpene isolated from *O. mexicana* must therefore be 3-oxo-28,29-dihydroxyolean-12-ene (**1**). Confirmation of this structure was obtained by assignment of the carbon resonances of **2** and **4** (Table 1).

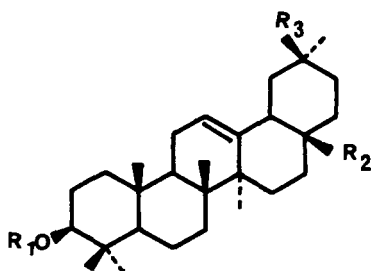
Other known compounds isolated from this species were: betulin, paniculatadiol ($3\beta,29$ -dihydroxyolean-12-ene) (**5**), and salaspermic acid (**6**).

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.— 1H - and ^{13}C -nmr spectra were obtained at 200



- 1 $R_1=O, R_2=H$
- 2 $R_1=O, R_2=Ac$
- 3 $R_1=\beta-OAc, R_2=Ac$



- 4 $R_1=Ac, R_2=R_3=CH_2OAc$
- 5 $R_1=Ac, R_2=CO_2H, R_3=CO_2Me$
- 6 $R_1=Ac, R_2=Me, R_3=CH_2OAc$

TABLE 1. ^{13}C -nmr Chemical Shifts of Compounds **2** and **4**

Carbon number	2	4	Carbon number	2	4
1	39.38 ^a	38.49	16	22.36	22.88
2	34.63	23.75	17	36.15	35.89
3	217.70	81.07	18	41.63	42.00
4	47.50	37.91	19	40.62	41.83
5	55.41	55.47	20	34.24	34.24
6	19.64	18.38	21	28.68	29.62
7	32.14	32.68	22	30.31	30.87
8	39.86	39.96	23	26.52	27.96
9	46.80	47.70	24	21.58	16.87
10	36.72	37.01	25	15.28	15.74
11	23.76	23.75	26	16.73	16.87
12	123.32	123.65	27	25.90	26.10
13	143.23	143.11	28	70.40	70.28
14	41.80	41.82	29	74.87	28.21
15	25.52	25.68	30	19.21	67.96

^appm (δ)

and 50 MHz, respectively, using CDCl_3 as the solvent. Ms were obtained at 70 eV in the electron impact mode. Ir were run in CHCl_3 . Voucher specimens (no. 7723) have been deposited at the Department of Biology, Technological Institute, Monterrey, Mexico.

ISOLATION OF THE TRITERPENES.—The methanolic extract (26 g) of the dried aerial parts of *O. mexicana* collected near Matamoros (Tamaulipas, Mexico) was chromatographed over silica gel and eluted with petrol-EtOAc mixtures affording, in order of elution, betulin (100 mg), paniculatadiol (10 mg), 3-oxo-28,29-dihydroxyolean-12-ene (**1**) (115 mg), salaspermic acid (40 mg), and orthosphenic acid (30 mg).

3-OXO-28,29-DIHYDROXYOLEAN-12-ENE

(**1**).—Ir ν max 3620, 3420, 2950, 2880, 1740, 1685, 1455, 1385, 1230, 1035, 1000 cm^{-1} ; ^1H nmr (60 MHz) δ 0.91, 0.99, 1.08 and 1.18 (each 3H, s), 1.05 (6H, s), 2.51 (2H, m), 3.25 and 3.59 (each 1H, d, $J=11$ Hz); 3.29 (2H, br s), 5.28 (1H, t); ms m/z 456(M^+) (2), 438(2), 426(10), 425(28), 408(2), 309(1), 250(11), 219(53), 201(100), 159(15), 145(18), 131(21).

DIACETATE **2**.—Ir ν max 3010, 2940, 2870, 1725, 1700, 1455, 1385, 1360, 1250, 1035, 908; ^1H nmr (60 MHz) δ 0.93, 1.01, 1.08 and 1.17 (each 3H, s), 1.06 (6H, s), 2.07 (6H, s), 2.49 (2H, m), 3.72 and 4.07 (each 1H, d, $J=11$ Hz), 3.76 (2H, br s), 5.28 (1H, t); ms m/z 540(M^+) (2), 480(14), 467(27), 420(6), 407(10), 321(4), 334(3), 274(20), 261(23), 214(17), 201(100), 199(16), 185(18), 159(16), 145(18).

REDUCTION AND ACETYLATION OF **2**.—The keto-diacetate **2** (25 mg) in THF (5 ml) was

treated with LiAlH_4 (27 mg) for 24 h. Several drops of EtOAc were added to eliminate the reagent before extraction with EtOAc in the usual way. The extract obtained by evaporation of the solvent was acetylated with $\text{Ac}_2\text{O}/\text{C}_5\text{H}_5\text{N}$ to afford **3**, mp 184°; ^1H nmr (60 MHz) δ 0.85 and 0.94 (each 6H, s), 1.15 (3H, s), 2.06 (9H, s), 3.71 and 4.08 (each 1H, d, $J=11$ Hz), 3.77 (2H, br s), 4.52 (1H, t), 5.26 (1H, t).

PREPARATION OF QUERATAROL TRIACETATE (**4**).—The dimethyl ester of serjanic acid (**5**) (200 mg) was reduced with LiAlH_4 as described previously (4). Acetylation of the triol obtained afforded **4** (80 mg); ^1H nmr (60 MHz) δ 0.87 (6H, s), 0.95 (9H, s), 1.17 (3H, s), 2.05 (6H, s), 3.75 and 4.05 (each 1H, d, $J=11$ Hz), 4.00 (2H, s), 4.52 (1H, t), 5.21 (1H, t).

PANICULATADIOL.—This product was isolated by acetylation and chromatography of several fractions of the main chromatography. Diacetate **6**: ^1H nmr (200 MHz) δ 0.82, 0.84, 0.85, 0.91, 0.94, 1.09 and 1.23 (each 3H, s), 2.03 and 2.04 (each 3H, s), 3.65 and 3.76 (each 1H, d, $J=10$ Hz), 4.50 (1H, t), 5.17 (1H, t); ms m/z 526(M^+) (4), 484(1), 466(11), 451(8), 406(1), 276(62), 249(7), 216(55), 201(27), 189(36), 187(22), 133(24).

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