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CLERODANE DITERPENOIDS FROM *POLYALTHIA LONGIFOLIA**

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Key Word Index—*Polyalthia longifolia*; Annonaceae; clerodane diterpenes; antifeedant activity.

Abstract—Two clerodane type diterpenoids, with antifeedant properties have been isolated from *Polyalthia longifolia* and identified as 16α-hydroxy-cleroda-3,13(14)*Z*-dien-15,16-olide and 16-oxo-cleroda-3,13(14)*E*-dien-15-oic acid on the basis of spectral properties. Configuration of the olide at C-16 was established by X-ray crystallographic analysis.

INTRODUCTION

Polyalthia longifolia Thw (Annonaceae) is a tall, handsome, evergreen tree cultivated in gardens all over India. Earlier work on *P. longifolia* reports isolation of proanthocyanidin trimer [1] and sitosterol [2] from the bark. In continuation of our work on screenin of plant species for pest control activity we found antifeedant activity in the acetone extract of leaves of *P. longifolia*. This note reports isolation and identification of two clerodane diterpenes **1** and **3**. X-ray analysis of the acetate (**2**) of **1** confirmed the stereochemistry at C-16.

RESULTS AND DISCUSSION

Air-dried leaves of *P. longifolia* were powdered and extracted with acetone. Chromatographic separation of the extract gave compounds **1** and **3**. Compound **1** (0.5%), $C_{20}H_{30}O_3$, exhibited four methyl signals; two tertiary, one secondary and one olefinic in the ^1H NMR spectrum (Table 1). The presence of hydroxy group (ν_{max} 3345 cm^{-1}) and β-substituted butenolide [(ν_{max} 1730, 1635 cm^{-1}; δH 5.83 (1H, *s*); δC 171 (*s*), 117 (*d*) and 172 (*s*) (Table 2)] was evident from spectral data and suggested a clerodane skeleton for **1**. A shift of a one proton singlet at δ6.04 in the spectrum of **1** to 6.84 on acetylation and the presence of doublets at δ99.69 and 94.04 in the ^{13}C NMR spectra of **1** and **2**, respectively, indicated the presence of a hydroxy group at the C-16 position. Compound **1**, therefore, was identified as 16-hydroxy-cleroda-3,13(14)*Z*-dien-15,16-olide. Single X-ray diffraction analysis of the crystalline acetate derivative (**2**) established an α-configuration for the hydroxyl at C-16. Finally, compound **1** was designated as 16α-hydroxy-3,13(14)*Z*-dien-15,16-olide.

The structure was solved by single crystal X-ray diffraction studies. Crystal data: crystals are monoclinic, space group $P2_1$, $Z=2$, with $a=8.963$ (2), $b=7.515$ (2), $c=15.323$ (1) Å, $\beta=97.38$ (1)°. The data were collected with a 4-circle automatic diffractometer using $MoK_\alpha(\lambda=0.7107$ Å). From 1651 independent reflections 1075 [$I>3\sigma(I)$] were considered as observed and used for structure solution. The structure was solved by direct methods [3] and refined by full matrix least squares refinement [4] in two blocks (anisotropic temperature factors for non-hydrogen atoms) with hydrogens in calculated positions which were confirmed by difference Fourier map. The isotropic temperature factors for hydrogen atoms were fixed. The final *R* factor was 0.065 after applying weights. The cyclohexene ring (ring A) has a 'half chair' and the cyclohexane ring (ring B) has a

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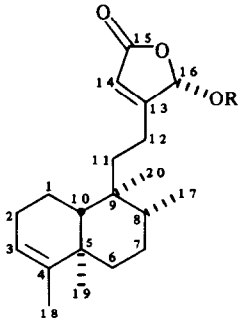

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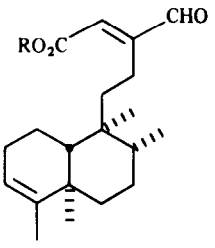
2 R = Ac



3 R = H
4 R = Me

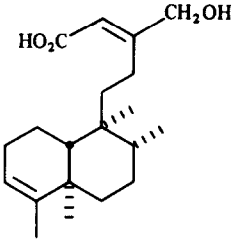


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Table 2. ^{13}C NMR shifts (δ ppm) of compounds **1**, **2** and **4**

C	1	2	4	C	1	2	4
1	18.06	17.93	17.93	11	27.62[b]	26.90[b]	27.47[b]
2	21.57	20.60	18.97	12	35.09	35.23	36.75
3	120.68	120.42	120.61	13	171	169.16	144.06
4	114.53	144.50	155.45	14	117.04	118.28	134.37
5	38.40[a]	38.34[a]	38.08[a]	15	172	164.99	165
6	26.97[b]	27.49[b]	26.67[b]	16	99.69	94.04	194
7	36.58	36.84	36.75	17	16.11	15.98	15.74
8	36.97	36.85	36.89	18	18.52	18.45	18.06
9	38.92[a]	38.86[a]	39.17[a]	19	18.20	18.13	17.83
10	46.79	46.72	46.41	20	20.08	20.01	19.79
						OCOMe	-OMe
						21.25	51.75
						OCOMe	
						168.19	

[a, b] Values in any vertical column may be interchanged

Table 1. ^1H NMR spectral data (δH ppm) of compounds **1–4**

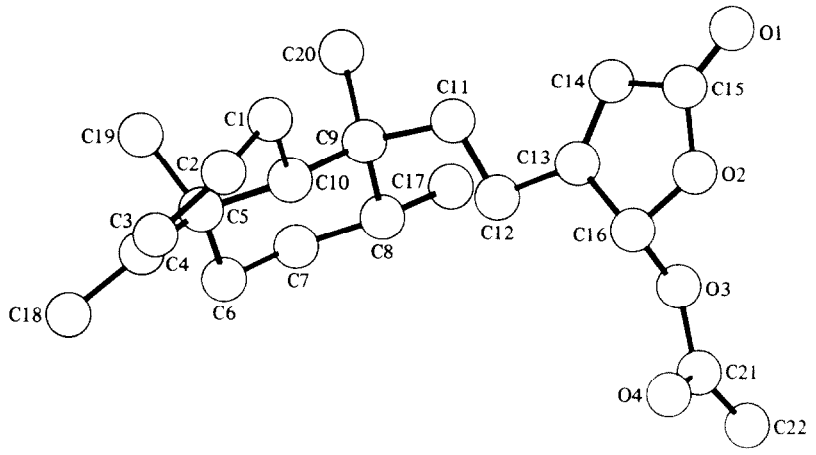
H	1	2	3	4
2	2.01 *br*	2.08 *br*	2.06 *br*	2.1 *br*
3	5.2 *br*	5.17 *br*	5.15 *br*	5.2 *br*
12	2.24 *m*	2.17 *m*	2.53 *t*	2.5 *m*
14	5.83 *s*	5.73 *s*	6.37 *s*	6.4 *s*
16	6.04 *s*	6.84 *s*	9.46 *s*	9.5 *s*
17	0.83 *d**	0.8 *d**	0.73 *d**	0.85 *d**
18	1.61 *d*†	1.57 *d*†	1.5 *d*†	1.58 *d*†
19	1.0	1.0 *s*	0.93 *s*	0.97 *s*
20	0.75 *s*	0.75 *s*	0.62 *s*	0.66 *s*
-OMe	—	—	—	3.8 *s*
-OAc	—	2.17 *s*	—	—

* $J = 7$ Hz.
† $J = 2$ Hz.

'chair' conformation. Since the torsion angles along the common C(5)–C(10) bond have opposite signs the two rings are *trans*-fused [5, 6]. A perspective view of the molecule is shown in Fig. 1. Full crystal data are deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K.

A literature survey revealed that Bohlmann and coworkers have recently reported 16,16-dihydroxylkolava-3,13(14)*Z*-dien-15-oic lactone with ambiguous configuration at C-16 from *Acritopappus longifolius* [7].

Compound **3** (1%), $C_{20}H_{30}O_3$, showed four methyl signals [δ0.62 (*s*), 0.93 (*s*), 0.73 (*d*) and 1.5 (*d*)] in its ^1H NMR spectrum similar to those in the spectrum of **1**. In the lower field region the 16-H singlet at δ6.04 in the spectrum of **1** was replaced by a singlet at δ9.46 in that of **3** and in the ^{13}C NMR spectrum of **1**, the 16-C doublet at δ99.69 was shifted to δ194 in the spectrum of **3** indicating replacement of hydroxyl by an aldehyde. The presence of



Perspective view of the molecule of compound **1**

Fig. 1.

α,β-unsaturated ester carbonyl as well as α,β-unsaturated aldehyde is revealed by peaks at ν_{max} 1740, 1710 and 1650 cm^{-1} in the IR spectrum of methyl ester **4**. Sodium borohydride reduction of **3** afforded a primary alcohol, 16-hydroxy cleroda-3,13(14)*E*-dien-15-oic acid (**5**), which failed to lactonize on treatment with tosic acid, confirming the *E*-configuration of the C-13 (14) double bond and it was found to be identical with the compound reported by Bohlmann [3]. Compound **3**, therefore, is identified as 16-oxocleroda-3,13(14)*E*-dien-15-oic acid.

Compounds **1** and **3** exhibited antifeedant activity against casterlooper (*Achaea janata*).

EXPERIMENTAL

^1H and ^{13}C NMR: at 90 MHz in $CDCl_3$ and TMS as internal standard, chemical shifts in ppm (δ). MS: 70 eV, direct inlet system.

Isolation of compounds **1** *and* **3**. Green leaves of *P. longifolia* were dried in the shade and powdered. The powdered material (1 kg) was extracted with Me_2CO (2 × 5 l) at room temp. The solvent was removed at 40°/30 mm Hg in a rotavapour to yield a dark green extract (100 g). The extract (50 g) was treated with petrol (2 × 250 ml) and the soluble portion (24 g) was chromatographed over silica gel. The column was successively eluted with petrol–EtOAc (9:1).[fraction A1 (5.6 g)], petrol–EtOAc (4:1) [fraction A2 (7 g) in earlier fractions and fraction A3 (6.65 g) in later fractions] and Me_2CO [fraction A4 (4.35 g)] Fr. A2 was extracted with $NaHCO_3$ soln which on treatment with conc. HCl gave compound **3**. After passing through activated charcoal compound **3** was obtained as a colourless gum (5 g 1%) $[\alpha]_D^{26}$ −70.58° (MeOH; *c* 0.0107). UV λ_{max}^{MeOH} 238 nm (ε 12935). IR ν_{max}^{Neat} cm^{-1}: 3345, 2920, 1730, 1635, 1435, 1125, 940. MS *m/z* (rel. int.): 318 $[M]^+$ (10), 303 (6), 285 (15), 190 (100), 189 (19), 175 (25), 161 (20), 135 (48). Treatment of **3** with CH_2N_2 yielded methyl ester **4** as a colourless gum $[\alpha]_D^{26}$ −90.9° (MeOH; *c* 0.088). UV λ_{max}^{MeOH} 238 nm (ε 9304). IR ν_{max}^{Neat} cm^{-1}: 2990, 1740, 1710, 1650, 1450, 1390, 1020, 910, 880. MS *m/z* (rel. int.): 332 $[M]^+$ (10), 317 (8), 301 (12), 285 (8), 203 (14), 191 (78), 190 (100), 189 (90), 175 (32), 135 (49), 121 (65), 107 (68), 95 (98). (Found: C, 75.58; H, 9.50 $C_{21}H_{32}O_3$ requires C, 75.86; H, 9.70%.)

Fr. A3 on repeated chromatography over silica gel afforded **1** as a colourless gum (2.5 g, 0.5%). $[\alpha]_D^{26}$ −70.58° (MeOH, *c* 0.0107). UV λ_{max}^{MeOH} 210 nm (ε 14163). IR ν_{max}^{Neat} cm^{-1}; 3345, 2920, 1730, 1635, 1435, 1125, 940, 750. MS *m/z* (rel. int.) 318 $[M]^+$ (8), 303 (5), 285 (12), 191 (40), 190 (100), 189 (15), 175 (22), 135 (48), 123 (60), 107 (88), 94 (99).

Acetylation of compound **1**. Compound **1** (1.2 g) in pyridine (10 ml) was treated with AC_2O (10 ml) and left at room temp. for 48 hr. The reaction mixture was poured into cold H_2O and extracted with EtOAc. The organic layer after washing with H_2O and brine was dried (Na_2SO_4) and evapd to give a semi-solid residue which was purified by chromatography over silica gel to give compound **2**, mp 175° (petrol + EtOAc) (0.92 g, 71%). $[\alpha]_D^{26}$ −24.24° (MeOH; *c* 0.066). IR ν_{max}^{Neat} cm^{-1}: 2900, 1760, 1640, 1450, 1380, 1200, 880, 725. MS *m/z* (rel. int.): 360 $[M]^+$ (1) 300 (27), 285 (88), 267 (13), 190 (40), 189 (100), 175 (40), 119 (40), 107 (61), 105 (58), 91 (53). (Found: C, 73.03; H, 9.12. $C_{22}H_{32}O_4$ requires C, 73.30; H, 8.95%.)

Reduction compound **3**. A soln of **3** (0.2 g) in EtOH (8 ml) was treated with $NaBH_4$ (0.08 g) at 5° and left overnight. The reaction mixture was diluted with cold H_2O and extracted with EtOAc. The organic layer was washed with brine and dried (Na_2SO_4). After removing solvent the residue was chromatographed to give 5 (0.1 g), mp 170° (petrol + C_6H_6). $[\alpha]_D^{26}$ −67.85° (MeOH; *c* 0.112). IR ν_{max}^{Neat} cm^{-1}: 3280, 2950, 1695, 1640, 1450, 1380, 1290, 900. ^1H NMR: δ0.75 (3H, *s*), 0.84 (3H, *d*, *J* = 7 Hz), 1.03 (3H, *s*) 1.59 (3H, *d*, *J* = 2 Hz), 2.06 (2H, *br*), 2.37 (2H, *m*), 4.18 (2H, *d*, *J* = 2 Hz), 5.15 (1H, *br*), 5.96 (1H, *s*). MS *m/z* (rel. int.): 320 $[M]^+$ (2). 305 (4), 191 (42), 175 (11), 163 (12), 149 (21), 135 (32), 121 (55), 107 (100), 95 (95). (Found: C, 75.21; H, 10.18; $C_{20}H_{32}O_3$ requires C, 74.96; H, 10.06%).

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