

3-Oxolup-20(29)-en-30-al, a New Lupane from *Gymnosporia emarginata* (Celastraceae) ¹

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The stem bark of *Gymnosporia emarginata* (Willd.) Hook f. ex. Thw. (Celastraceae) contains a number of triterpenes including a new oxygenated lupane, 3-oxolup-20(29)-en-30-al (1) and two related lupanes, 3 β -hydroxylup-20(29)-en-30-al (2) and 30-hydroxylup-20(29)-en-3-one (3). The structures of these compounds have been established by spectroscopic and chemical methods.

GYMNOSPORIA EMARGINATA (Willd.) Hook f. ex. Thw. (Celastraceae) is a shrub growing in the dry zone of Sri Lanka. Previous work on the genus *Gymnosporia* include the isolation of quinonoid triterpene, oleanane, lupane, and long-chain hydrocarbon derivatives from *G. rothiana*,² *G. ovata*,³ *G. wallichiana*,⁴ and *G. montana*.⁵ Several lupane derivatives have been isolated from the Celastraceae.^{1,6-9}

RESULTS AND DISCUSSION

The benzene extract of the dried, ground bark of *Gymnosporia emarginata* collected in Amaduwa, near Hambantota, Sri Lanka contained a number of triterpenes including the three lupane derivatives 3-oxolup-20(29)-en-30-al (1), 3-hydroxylup-20(29)-en-30-al (2), and 30-hydroxylup-20(29)-en-3-one (3). β -Amyrin which was the major constituent, β -amyrenone, sitosterol, and pristimerin were identified by comparison with authentic material. The physical and spectroscopic data of yet another oleanane derivative were identical to those reported for 3,11-dioxo-olean-12-ene, previously isolated from *Gymnosporia rothiana* Laws.²

The structures of the three lupanes were elucidated using spectroscopic and chemical methods. Two of the lupanes absorbed in the u.v. region with λ_{max} at 225 nm, indicating the presence of an $\alpha\beta$ unsaturated carbonyl group. They also contained aldehyde proton signals (δ ca. 9.5) in their ¹H n.m.r. spectra (Table). The presence of singlets at δ ca. 6.3 and ca. 5.9 for the vinyl

protons in both lupanes suggested that the double bond was part of a CH₂=CR-CHO system. The more polar lupane aldehyde (2) showed carbonyl absorption at 1 695 cm⁻¹ and OH absorption at 3 550—3 150 cm⁻¹ in its i.r. spectrum and was oxidised with chromium trioxide-pyridine to the less polar aldehyde (1). Huang-Minlon reduction of the aldehyde (1) gave the lupene (10), suggesting the presence of a lupane skeleton with the $\alpha\beta$ unsaturated aldehyde group in the side-chain in both aldehydes (1) and (2).

The third lupane isolated from the extract did not absorb in the u.v. region but its i.r. spectrum showed carbonyl and OH absorptions at 1 710 and 3 550—3 150 cm⁻¹, respectively. Oxidation of this lupane alcohol (3) with chromium trioxide-pyridine gave the aldehyde (1), indicating that the OH group was allylic to the double bond of the lupene side-chain. The broad singlet at δ 4.05 due to two protons in the ¹H n.m.r. spectrum of the alcohol (3) was evidence for the hydroxy-group being primary.

Acetalisation of the alcohol (3) with ethylene glycol gave the acetal (6) which was oxidised with chromium trioxide-pyridine to the aldehyde (7). Deacetalisation of the aldehyde (7) gave the aldehyde (1) while Huang-Minlon reduction of the aldehyde (7) gave the acetal (8). Refluxing the acetal (8) with toluene-*p*-sulphonic acid in acetone gave lupenone (9), providing evidence for the carbonyl group at C-3 (Scheme).

The aldehyde (1) must therefore have the structure

TABLE
¹H N.m.r. data (CCl₄, 60 MHz) (J/Hz or W_{1/2}/Hz in parentheses)
Compound

	(1)	(2)*	(3)	(4)*	(5)	(6)	(7)	(8)
3 α -H		3.25 (dd, J 6, 9)		3.18 (dd, J 6, 10)				
29-H	6.23	6.32	4.90 (m, W _{1/2} 6)	4.90 (m, W _{1/2} 4)	4.88 (m, W _{1/2} 4)	4.92 (m, W _{1/2} 4)	6.17	4.67 (m, W _{1/2} 6)
29'-H	5.86	5.93	4.90 (m, W _{1/2} 6)	4.90 (m, W _{1/2} 4)	4.88 (m, W _{1/2} 4)	4.92 (m, W _{1/2} 4)	5.80	4.54 (m, W _{1/2} 6)
30-H	9.53	9.57	4.05 (s, W _{1/2} 4)	4.15 (m, W _{1/2} 4)	4.48 (s, W _{1/2} 4)	4.05 (s, W _{1/2} 3)	9.47	1.67 (s, W _{1/2} 6)
OAc					2.03			
O[CH ₂] ₂ O						3.92	3.87	3.87
Methyls	1.08	1.06	1.08	1.03	1.07	1.03	1.03	1.03
	1.03	1.03	1.05	1.00	1.01	1.00	0.96	1.00
	1.00	0.98	1.00	1.00	0.97	0.87	0.83	0.87
	0.93	0.95	0.97	0.87	0.97	0.87	0.83	0.87
	0.93	0.83	0.93	0.77	0.92	0.77	0.83	0.79
	0.83	0.78	0.80	0.77	0.78	0.77	0.76	0.77

* In CDCl₃.

alcohol (3) (0.4 g) was refluxed with toluene-*p*-sulphonic acid (40 mg) and ethylene glycol (0.8 g) in dry benzene (40 ml) for 90 min using a Dean-Stark apparatus to remove water. The usual work-up followed by purification with p.l.c. [CHCl₃-MeOH (99:1) × 1] gave 3,3-ethylenedioxy-lup-20(29)-*en*-30-*ol* (6) (0.3 g), colourless needles from light petroleum, m.p. 195–196 °C, $[\alpha]_D -15^\circ$ (*c* 0.1) (Found: C, 78.3; H, 11.1%. C₃₂H₅₂O₃ requires C, 78.3; H, 10.9%); ν_{\max} 3 390, 1 200, 1 105, 1 090, and 1 050 cm⁻¹; *m/e* 484 (*M*⁺, 40%), 469 (15), (422 (16), 384 (65), 219 (32), 215 (30), 201 (60), 100 (95), and 99 (100).

3,3-Ethylenedioxy-lup-20(29)-*en*-30-*al* (7).—The acetal (6) (0.3 g) was stirred for 18 h with CrO₃ (120 mg) in pyridine (6 ml). The usual work-up followed by p.l.c. (CHCl₃ × 1) gave the less polar product, 3,3-ethylenedioxy-lup-20(29)-*en*-30-*al* (7) (150 mg), colourless needles from CHCl₃, m.p. 200–202 °C, $[\alpha]_D -20^\circ$ (*c* 0.1) (Found: C, 79.2; H, 10.4. C₃₂H₅₀O₃ requires C, 79.6; H, 10.4%); λ_{\max} 225 nm (log ϵ 3.84); ν_{\max} 1 690, 1 200, 1 150, 1 115, 1 100, and 1 060 cm⁻¹; *m/e* 480 (*M*⁺, 20%), 467 (12), 382 (42), 339 (11), 249 (9), 217 (42), 203 (43), and 99 (100).

3,3-Ethylenedioxy-lup-20(29)-*ene* (8).—The acetal (7) (150 mg) was reduced under Huang-Minlon conditions by refluxing for 3 h with ethylene glycol (10 ml), N₂H₄·H₂O (1 g) and KOH (200 mg), distilling to 200 °C, and then refluxing for a further 3 h. The usual work-up followed by p.l.c. [light petroleum-benzene (1:9) × 1] gave 3,3-ethylenedioxy-lup-20(29)-*ene* (8) (50 mg), needles from CHCl₃-MeOH, m.p. 195–197 °C, $[\alpha]_D +3.3^\circ$ (*c* 0.1) (Found: C, 81.8; H, 11.3. C₃₂H₅₂O₂ requires C, 82.0; H, 11.2%); ν_{\max} 1 200, 1 145, 1 115, 1 100, and 1 050 cm⁻¹; *m/e* 468 (*M*⁺, 21%) 453 (10), 424 (6), 368 (42), 325 (18), 249 (9), 245 (11), 203 (6), 100 (95), and 99 (100).

Lup-20(29)-*en*-3-*one* (9).—The acetal (8) (35 mg) was refluxed for 12 h with toluene-*p*-sulphonic acid (35 mg) in acetone (35 ml). The usual work-up gave colourless needles (30 mg) from EtOH, m.p. 169–170 °C, $[\alpha]_D +58.3^\circ$ (*c* 2.0) (lit.⁸ m.p. 170 °C, $[\alpha]_D +64^\circ$), identical with an authentic sample of lup-20(29)-*en*-3-*one* (9) (mixed m.p. and i.r.).

Reduction of the Acetal (7).—The acetal (7) (25 mg) was refluxed with LiAlH₄ (20 mg) in Et₂O (20 ml) for 1 h. The usual work-up gave colourless needles (20 mg) from light petroleum, m.p. 195–196 °C, identical with the alcohol (6).

Reduction of the Aldehyde (1).—The aldehyde (1) (50 mg) was reduced under the Huang-Minlon conditions described

earlier with ethylene glycol (7 ml), N₂H₄·H₂O (1 g), and KOH (70 mg). The usual work-up gave colourless needles (24 mg) from CHCl₃-MeOH, m.p. 162–163 °C, $[\alpha]_D +28^\circ$ (*c* 2.0) (lit.⁸ m.p. 163 °C, $[\alpha]_D +30^\circ$), identical with authentic lup-20(29)-*ene* (10).

Lup-20(29)-*ene*-3 β ,30-*diol* (4).—The alcohol (3) (30 mg) was refluxed for 1 h with LiAlH₄ (25 mg) in Et₂O (20 ml). The usual work-up gave, on recrystallisation from CHCl₃-MeOH, lup-20(29)-*ene*-3 β ,30-*diol* (4) (27 mg), m.p. 234–235 °C, $[\alpha]_D -16^\circ$ (*c* 1.0) (lit.⁶ m.p. 235–236°, $[\alpha]_D -8^\circ$); ν_{\max} 3 330 cm⁻¹; *m/e* 442 (*M*⁺, 20%), 424 (13), 409 (11), 384 (6), 344 (33), 315 (18), 234 (25), 220 (25), 207 (100), 203 (38), and 189 (85).

Acetylation of 30-Hydroxy-lup-20(29)-*en*-3-*one* (3).—The alcohol (3) (20 mg) was treated with Ac₂O-pyridine (1:1) (2 ml) for 5 min and then extracted with CHCl₃. Concentration followed by separation by p.l.c. [CHCl₃-MeOH (99:1) × 1] gave a colourless oil (18 mg), $[\alpha]_D -12.2^\circ$ (*c* 1.5); ν_{\max} (Nujol) 1 740, 1 705, and 1 230 cm⁻¹.

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