

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

By Dharmassree B. T. Wijeratne, Vijaya Kumar,* and M. Uvais S. Sultanbawa, Department of Chemistry, University of Peradeniya, Peradeniya, Sri Lanka

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).

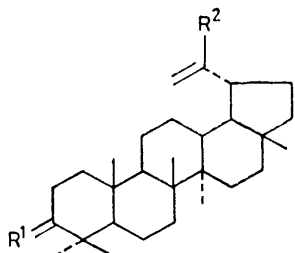
The aldehyde (1) must therefore have the structure

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

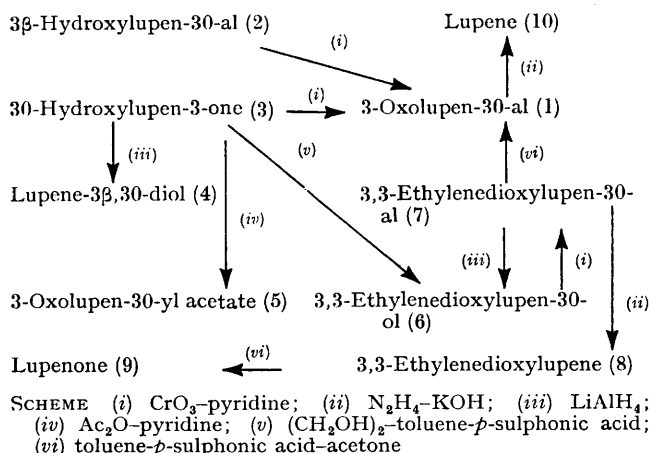
	(1)	(2)*	(3)	(4)*	(5)	(6)	(7)	(8)
3 α -H		3.25 (dd, J 6, 9)		3.18 (dd, J 6, 10)				
29-H	6.23	6.32	4.90 (m, W _{1/2} 6)	4.90 (m, W _{1/2} 4)	4.88 (m, W _{1/2} 4)	4.92 (m, W _{1/2} 4)	6.17	4.67 (m, W _{1/2} 6)
29'-H	5.86	5.93	4.90 (m, W _{1/2} 6)	4.90 (m, W _{1/2} 4)	4.88 (m, W _{1/2} 4)	4.92 (m, W _{1/2} 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.

shown, 3-oxolup-20(29)-en-30-al, a new lupane derivative, while the aldehyde (2) must be 3 β -hydroxylup-20(29)-en-30-al, and its physical and spectroscopic data are identical to those reported for the compound of that structure isolated from *Quercus championii*.⁶ The alcohol (3), m.p. 186–187 °C, must have the structure 30-hydroxylup-20(29)-en-3-one, and its i.r. and n.m.r.



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| (1) R ¹ = O, R ² = CHO | (6) R ¹ = O(CH ₂) ₂ O, R ² = CH ₂ OH |
| (2) R ¹ = β -OH, α -H, R ² = CHO | (7) R ¹ = O(CH ₂) ₂ O, R ² = CHO |
| (3) R ¹ = O, R ² = CH ₂ OH | (8) R ¹ = O(CH ₂) ₂ O, R ² = Me |
| (4) R ¹ = β -OH, α -H, R ² = CH ₂ OH | (9) R ¹ = O, R ² = Me |
| (5) R ¹ = O, R ² = CH ₂ OAc | (10) R ¹ = 2H, R ² = Me |



spectra agreed closely with those reported for an oil isolated from *Flourensia heterolepis*, for which this structure was proposed.⁷ Both lupanes have been isolated for the first time from the family Celastraceae, although a closely related lupanediol, lup-20(29)-ene-3 β ,30-diol (4) has been isolated from *G. wallichiana*.⁴

Lithium aluminium hydride reduction of the alcohol (3) gave the diol (4), with physical and spectroscopic properties identical to those reported. Analytical and spectral (¹H n.m.r. and m.s.) data were in agreement with the above structural assignments.

EXPERIMENTAL

M.p.s were recorded on a Kofler hot-stage apparatus. I.r. spectra were determined for KBr discs on a Perkin-Elmer 257 spectrophotometer, while u.v. spectra were recorded in EtOH solutions on a Pye-Unicam SP 8000

spectrophotometer. ¹H N.m.r. spectra were measured on a Varian T60 spectrometer in CDCl₃ and CCl₄ solutions using SiMe₄ as internal standard (see Table). Optical rotations were measured in CHCl₃ solution at 25 °C on a Perkin-Elmer 141 polarimeter. Microanalyses and mass spectral studies were carried out at Ciba-Geigy Ltd., Basle. Light petroleum refers to the fraction of b.p. 40–60 °C. P.l.c. was carried out on Merck silica gel PF₂₅₄ + PF₃₆₆.

The stem bark of *Gymnosporia emarginata* (1 kg) collected in Amaduwa, near Hambantota, Sri Lanka was dried, ground, and extracted with benzene to give the extract (22 g). This extract (22 g) was chromatographed on silica (550 g) to give, on elution with light petroleum-CHCl₃ (9:1) and light petroleum-CHCl₃ (1:4) respectively β -amyrenone (55 mg), colourless needles from CHCl₃-MeOH, m.p. 177–178 °C, [α]_D +105° (lit.,⁸ m.p. 177–179 °C, [α]_D +107°) and β -amyrene (1.35 g), colourless needles from light petroleum, m.p. 196–197 °C, [α]_D +89.2° (lit.,⁸ m.p. 197–197.5 °C, [α]_D +88°), both found to be identical on comparison with authentic material (mixed m.p. and i.r.).

3-Oxolup-20(29)-en-30-al (1).—Further elution with CHCl₃ followed by p.l.c. [CHCl₃-MeOH (99:1) \times 1] gave on work-up the less polar compound 3-oxolup-20(29)-en-30-al (1), colourless needles from MeOH, m.p. 193–194 °C, [α]_D +30.8° (c 3.0) (Found: C, 82.1; H, 10.5. C₃₀H₄₆O₂ requires C, 82.1; H, 10.6%); λ_{\max} , 225 nm (log ϵ 3.85); ν_{\max} , 1705 and 1685 cm⁻¹; *m/e* 438 (*M*⁺, 46%), 423 (15), 405 (8), 341 (14), 220 (20), 219 (47), 205 (100), 203 (58), 201 (30), and 149 (35); and then the more polar compound sitosterol (0.25 g), colourless needles from MeOH, m.p. 136–137 °C, [α]_D -35° (lit.,⁸ m.p. 136–137 °C, [α]_D -35°), identical with authentic material.

30-Hydroxylup-20(29)-en-3-one (3).—Elution with CHCl₃ followed by recrystallisation from light petroleum gave colourless plates of 30-hydroxylup-20(29)-en-3-one (3) (1.1 g), m.p. 186–187 °C [α]_D +21.2° (c 3.0) (lit.,⁷ colourless oil) (Found: C, 81.5; H, 11.1. C₃₀H₄₈O₂ requires C, 81.8; H, 11.0%); ν_{\max} , 3410 and 1705 cm⁻¹; *m/e* 440 (*M*⁺, 52%), 422 (14), 407 (10), 382 (20), 313 (45), 245 (25), 234 (14), 221 (40), 205 (100), 189 (32), and 148 (40).

3 β -Hydroxylup-20(29)-en-30-al (2).—Elution with CHCl₃ followed by p.l.c. [CHCl₃-MeOH (49:1) \times 1] gave on work-up the less polar compound, 3,11-dioxo-olean-12-ene (0.2 g), colourless plates from MeOH, m.p. 240–243 °C with sintering at 230 °C, [α]_D +144° (c 2.0) (lit.,² m.p. 241–245°, [α]_D +144°); λ_{\max} , 251 nm (log ϵ 4.09); ν_{\max} , 1715, 1655, and 1625 cm⁻¹; δ 0.90 (s, 9 H), 1.07, 1.1, 1.18, 1.27, and 1.37 (all s, each 3 H), 2.45 (br s, *W*_{1/2} 4 Hz), and 5.67 (br s, *W*_{1/2} 2 Hz); and the more polar compound, 3 β -hydroxylup-20(29)-en-30-al (2) (20 mg), colourless needles from light petroleum, m.p. 234–235 °C, [α]_D +2.5 (c 1.0) (lit.,^{4b} m.p. 240 °C, lit.,⁶ m.p. 234–235 °C, [α]_D +3°); λ_{\max} , 225 nm (log ϵ 3.85); ν_{\max} , 3300 and 1695 cm⁻¹. Further elution with CHCl₃-MeOH (99:1) gave on purification by p.l.c. [CHCl₃-MeOH (49:1)] pristimerin (230 mg), orange needles from MeOH, m.p. 213–214 °C, [α]_D -164° (c 1.0) (lit.,⁹ m.p. 214–217 °C), found to be identical on comparison with authentic material (mixed m.p. and i.r.).

Oxidation of 30-Hydroxylup-20(29)-en-3-one (3).—The alcohol (3) (30 mg) was oxidised with CrO₃ (20 mg) in pyridine (2 ml) during 18 h. Work-up gave colourless needles from MeOH, m.p. 193–194 °C, identical with 3-oxolup-20(29)-en-30-al (1).

Acetalisation of 30-Hydroxylup-20(29)-en-3-one (3).—The

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. [$\text{CHCl}_3\text{-MeOH}$ (99:1) \times 1] gave 3,3-ethylenedioxy $\text{lup-20(29)-en-30-ol}$ (6) (0.3 g), colourless needles from light petroleum, m.p. 195–196 °C, $[\alpha]_{\text{D}} -15^\circ$ (*c* 0.1) (Found: C, 78.3; H, 11.1%). $\text{C}_{32}\text{H}_{52}\text{O}_3$ 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 $\text{lup-20(29)-en-30-al}$ (7).—The acetal (6) (0.3 g) was stirred for 18 h with CrO_3 (120 mg) in pyridine (6 ml). The usual work-up followed by p.l.c. ($\text{CHCl}_3 \times 1$) gave the less polar product, 3,3-ethylenedioxy $\text{lup-20(29)-en-30-al}$ (7) (150 mg), colourless needles from CHCl_3 , m.p. 200–202 °C, $[\alpha]_{\text{D}} -20^\circ$ (*c* 0.1) (Found: C, 79.2; H, 10.4). $\text{C}_{32}\text{H}_{50}\text{O}_3$ requires C, 79.6; H, 10.4%); λ_{max} 225 nm ($\log \epsilon$ 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), $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (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) \times 1] gave 3,3-ethylenedioxy lup-20(29)-ene (8) (50 mg), needles from $\text{CHCl}_3\text{-MeOH}$, m.p. 195–197 °C, $[\alpha]_{\text{D}} +3.3^\circ$ (*c* 0.1) (Found: C, 81.8; H, 11.3). $\text{C}_{32}\text{H}_{52}\text{O}_2$ 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).

$\text{lup-20(29)-en-3-one}$ (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, $[\alpha]_{\text{D}} +58.3^\circ$ (*c* 2.0) (lit.,⁸ m.p. 170 °C, $[\alpha]_{\text{D}} +64^\circ$), identical with an authentic sample of $\text{lup-20(29)-en-3-one}$ (9) (mixed m.p. and i.r.).

Reduction of the Acetal (7).—The acetal (7) (25 mg) was refluxed with LiAlH_4 (20 mg) in Et_2O (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), $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ (1 g), and KOH (70 mg). The usual work-up gave colourless needles (24 mg) from $\text{CHCl}_3\text{-MeOH}$, m.p. 162–163 °C, $[\alpha]_{\text{D}} +28^\circ$ (*c* 2.0) (lit.,⁸ m.p. 163 °C, $[\alpha]_{\text{D}} +30^\circ$), identical with authentic lup-20(29)-ene (10).

$\text{lup-20(29)-ene-3\beta,30-diol}$ (4).—The alcohol (3) (30 mg) was refluxed for 1 h with LiAlH_4 (25 mg) in Et_2O (20 ml). The usual work-up gave, on recrystallisation from $\text{CHCl}_3\text{-MeOH}$, $\text{lup-20(29)-ene-3\beta,30-diol}$ (4) (27 mg), m.p. 234–235 °C, $[\alpha]_{\text{D}} -16^\circ$ (*c* 1.0) (lit.,⁶ m.p. 235–236°, $[\alpha]_{\text{D}} -8^\circ$); 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 $\text{lup-20(29)-en-3-one}$ (3).—The alcohol (3) (20 mg) was treated with Ac_2O -pyridine (1:1) (2 ml) for 5 min and then extracted with CHCl_3 . Concentration followed by separation by p.l.c. [$\text{CHCl}_3\text{-MeOH}$ (99:1) \times 1] gave a colourless oil (18 mg), $[\alpha]_{\text{D}} -12.2^\circ$ (*c* 1.5); ν_{max} (Nujol) 1 740, 1 705, and 1 230 cm^{-1} .

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