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CYCLOART-25-EN-3β-OL FROM *EUPHORBIA NIVULIA**

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Key Word Index—*Euphorbia nivulia*; Euphorbiaceae; tetracyclic triterpenes; cycloart-25-en-3β-ol; cyclolaudenol.

Abstract—A new tetracyclic triterpene cycloart-25-en-3β-ol (9β,19-cyclolanost-25-en-3β-ol) and cyclolaudenol, have been isolated from *Euphorbia nivulia*.

INTRODUCTION

Euphorbia nivulia Buck-Ham and *E. nerifolia* Linn resemble one another very closely except in the cross section of their stem, the former being circular and the latter being pentangular. The present investigation reveals that the triterpene composition can be used as a tool to differentiate the two plants. The latex revealed the presence of a new tetracyclic triterpene, cycloart-25-en-3β-ol, and cyclolaudenol. The stem contained cyclolaudenol and sitosterol. The leaves afforded sitosterol. None of these compounds was reported in *E. nerifolia* [1–4]. The leaves and the latex of *E. nivulia* are used in the Ayurvedic system of medicine for bronchitis and rheumatism [5].

RESULTS AND DISCUSSION

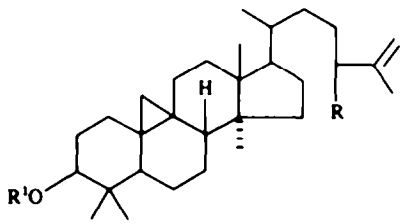
The alcoholic extract of the latex of *E. nivulia* produced a colourless solid (2%), which was resolved into two crystalline components, cycloart-25-en-3β-ol (**1**) and cyclolaudenol (**2**), and a viscous complex mixture, by CC over neutral alumina. The mass spectrum of **1** showed a $[M]^+$ at *m/z* 426 ($C_{30}H_{50}O$) and it had fragment ions at *m/z* 339 $[(M-18)-69]^+$, 315 [M − 111 (entire substituent at C-17)]$^+$, 286 [M − 140 (loss of ring A along with C-6 and C-19)]$^+$, 111 (side chain C_8H_{15}) and 69 (base peak, C_5H_9). The ^{1}H NMR spectrum of **1** showed signals at δ0.48 and 0.70 (2H, AB doublets, J = 5 Hz, cyclopropane ring), 0.87–1.65 (18H, 6 Me) and 4.70 (2H, $-C=CH_2$). The IR spectrum of **1** showed bands at 3445 (hydroxyl), 3045 (methylene group of cyclopropane bridge), 1370, 1360 (geminal dimethyls) and 880 cm^{-1} (terminal methylene group).

Catalytic hydrogenation of **1** gave a dihydro compound (**4**) the physical characteristics of which were in complete agreement with cycloartanol [7, 8]. The mass spectrum of **4** showed a $[M]^+$ at *m/z* 428 ($C_{30}H_{52}O$). The major mass fragments in the mass spectrum of **4** were at *m/z* 367, 341, 315 and 288, identical with those reported in the mass spectrum of cycloartanol [7]. The ^{1}H NMR spectrum of **4** showed signals at δ0.48 and 0.70 (2H, AB doublets, J = 5 Hz, cyclopropane ring), 0.87–1.65 (21H, 7 Me). The IR spectrum of **4** showed bands at 3445 (hydroxyl), 3045 (methylene group of cyclopropane bridge), 1370 and 1360 cm^{-1} (geminal dimethyls). Hence, it was concluded that compound **1** was cycloart-25-en-3β-ol. The spectral data and direct comparison with an authentic sample confirms the identity of **2** as cyclolaudenol [6].

The benzene extract of the leaves produced a colourless sticky mass which, on CC over alumina, yielded sitosterol (0.09%) and an unresolvable complex mixture. The benzene extract of the stem gave a light-green sticky mass which, on CC over silica gel gave cyclolaudenol (0.15%), sitosterol (0.03%) and an unresolvable complex mixture.

EXPERIMENTAL

Mps are uncorr. ORD were measured in $CHCl_3$. IR spectra were recorded in KBr and Nujol and ^{1}H NMR spectra were measured in $CDCl_3$ with TMS as int. standard. Brockmann



1 R = H, R¹ = H
2 R = Me, R¹ = H
3 R = H, R¹ = Ac

* Part II in the series "Chemistry of Euphorbiaceae". For Part I see ref. [6].

alumina and silica gel (less than 200 mesh, Acme) were used as the adsorbents for chromatography.

Extraction and isolation. The latex, leaves and stem of *E. nivulia* Buck-Ham (MRL No. 3500; Mycology Research Laboratory, V. V. College, Hyderabad, India), were collected from Kondapalli near Vijayawada, Andhra Pradesh, India. The coagulated latex (250 g) of *E. nivulia* was refluxed with EtOH (3 × 0.5 l.) for 12 hr. and the mixture filtered hot. The combined extract (1.5 l.), on removal of the solvent, gave a colourless solid (5 g). This was adsorbed over a column of neutral Al_2O_3 (300 g) and eluted with petrol (1 l.), C_6H_6 (2 l.) and $CHCl_3$ (2 l.). The petrol eluate gave a viscous complex mixture (0.5 g). The C_6H_6 eluate gave a colourless solid (1.5 g), homogeneous on TLC which crystallized from petrol to give colourless needles of **1**. Further elution with $CHCl_3$ gave a colourless solid (3 g) homogeneous on TLC, which crystallized from MeOH to yield colourless needles of **2**.

The dry powdered leaves (200 g) of *E. nivulia* were extracted with C_6H_6 in a Soxhlet extractor for 24 hr. The extract (2 l.), on removal of the solvent, furnished a yellowish sticky mass (5 g). It did not contain any acidic compound (10% NaOH). It was adsorbed over a column of silica gel (200 g) and eluted with petrol (1 l.) and C_6H_6 (2 l.). The petrol eluate did not give any compound, whereas the C_6H_6 eluate gave sitosterol (identity confirmed by comparison with an authentic sample) and an unresolvable complex mixture.

The dry powdered stems (2 kg) of *E. nivulia* were refluxed with C_6H_6 (3 × 3 l.) for 24 hr and the mixture was filtered while hot. The extract, on removal of the solvent, furnished a greenish sticky mass (10 g) which was adsorbed over a column of silica gel (500 g) and eluted with C_6H_6 (3 × 1 l.) and, finally, with $CHCl_3$ (2 l.). The C_6H_6 eluate yielded cyclolaudenol (**2**) (5 g) and the $CHCl_3$ eluate gave sitosterol (500 mg) and an unresolvable complex mixture (2 g).

Cycloart-25-en-3β-ol (**1**). Mp 85°; $[\alpha]_D$ + 23° ($CHCl_3$; *c* 0.926); MS *m/z* (rel. int.): 426 $[M]^+$ (63.8), 339 (55.5), 315 (22), 286 (26), 111 (27), 69 (100).

Hydrogenation of **1**. Catalytic hydrogenation of **1** (Pd–C/H_2), purification by CC over Al_2O_3 and crystallization from EtOH, furnished the dihydro compound, cycloartanol (**4**): mp 100°; $[\alpha]_D$ + 50° ($CHCl_3$; *c* 1.016) (lit. [8] mp 101–102°; $[\alpha]_D$ + 51°). Acetate (**3**): semi-solid; $[\alpha]_D$ + 26° ($CHCl_3$; *c* 0.89); IR ν_{max}^{Nujol} cm^{-1}: 3045, 1725, 825.

Cyclolaudenol (**2**). Mp 125°; $[\alpha]_D$ + 46° ($CHCl_3$; *c* 1.005); MS *m/z* 440 $[M]^+$ (calc. for $C_{31}H_{52}O$); ^1H NMR: δ0.48, 0.70 (2H, AB doublets, *J* = 5 Hz cyclopropane ring), 0.87–1.65 (21H, 7 Me), 4.7 (2H, $>C=CH_2$); MS *m/z* (rel. int.): 440 $[M]^+$ (85), 425 $[M-Me]^+$ (40), 422 $[M-H_2O]^+$ (85), 407 (52), 379 (20), 353 (30), 315 (25), 300 (100), 175 (70); IR ν_{max}^{Nujol} cm^{-1}: 3450 (OH), 3055 (cyclopropane ring), 1730, 1360 (geminal dimethyls), 880 (terminal methylene group) [lit. [6, 9] mp 125°; $[\alpha]_D$ + 46° (identity confirmed by direct comparison with authentic sample [6])].

Sitosterol. Mp 134°; $[\alpha]_D$ − 34° [lit. [10] mp 136–137°; $[\alpha]_D$ − 36° (identity confirmed by direct comparison with authentic sample)].

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