

CYCLOROYLENOL, A CYCLOPROPANE CONTAINING EUPHOID FROM EUPHORBIA ROYLEANA*

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Abstract . Cycloroylenol, a new tetracyclic triterpene in the latex of Euphorbia royleana Boiss is shown to have structure (1a)

Currently, a great deal of interest centres around latex of euphorbia species as a possible petroleum substitute. The Himalayan plant Euphorbia royleana Boiss contains a large quantity of latex and some of its constituents have already been reported¹⁾. We now wish to describe the structure elucidation of the first cyclopropane containing compound 1a in the euphoids from this plant.

The alcohol isolated from the dried latex²⁾ was purified as the acetate by IDCC³⁾ on SiO₂-AgNO₃ and given the trivial name of cycloroylenyl acetate.

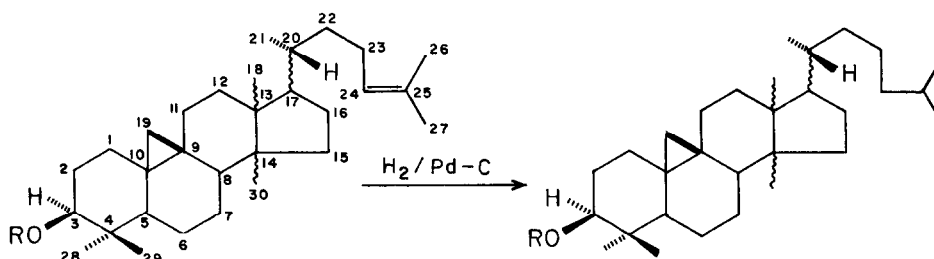
Cycloroylenyl acetate (1b), m.p. 120-122°, (α)_D^{29°} + 60.24°, (CHCl₃, \underline{c} : 0.644), was shown to contain CHOAc [IR(Nujol) \underline{Ca} 1735 and 1240 cm⁻¹], MS m/e (%): 468 (M⁺; 66), 453 (39), 409(100), 393(66), 366(45), 339(52), 286(81), 69(94) and 43(90); calcd. for C₃₂H₅₂O₂: M⁺, 468.74
¹HNMR: 0.83(3H, s, C₄ β -Me); 0.97 (3H, s, C₄ α -Me), 0.44 (2H, ABdd, δ_A = 0.33, δ_B = 0.56, C₁₉-H₂); 0.88(9H, s, C₁₃-Me, C₁₄-Me and C₂₀-Me); 2.05 (3H, s, C₃-OAc); 1.6 and 1.7 (3H, s, 3H, s, C₂₆ and C₂₇ di - Me); 4.58(1H, m 3 α -CH); 5.08(1H, t, = C₂₄-H). Cycloroylenyl acetate (1b) on hydrolysis [alcoholic KOH (10%)] gave cycloroylenol (1a), m.p. 103-105° (α)_D^{29°} + 33.17°, (CHCl₃, \underline{c} : 0.168) gave IR(Nujol): \underline{Ca} 3350 and 1099 cm⁻¹ for CHOH, analysed for C₃₀H₅₀O (M⁺ 426). ¹HNMR: 0.81 (3H, s, C₄-Me); 1.01 (3H, s, C₄ α -Me); 0.44 (2H, ABdd, δ_A = 0.3, δ_B = 0.58, C₁₉-H₂); 0.77

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(3H, s, C₁₃-Me); 0.88 (3H, s, C₁₄-Me); 0.97 (3H, s, C₂₀-Me); 1.6 and 1.69 (3H, s; 3H, s, C₂₆ and C₂₇ di-Me); 3.24 (1H, m, 3-H); 5.08 (1H, t, = C₂₄-H).

The mass fragmentation pattern of the compound 1b is consistent⁴⁾ with the fragmentation patterns observed in the acetates of tetracyclic triterpenoids. Initially it was conceived that cycloroylenol was cycloartenol. However, after preparation of several derivatives (2 - 4), it was obvious that these compounds are different from 6 - 8 derived⁵⁾ from cycloartenol (Scheme 1). Furthermore, an examination of the position of the C₁₃ methyl signal of the pairs 1a/5a (0.77/0.96); 2/6 (0.74/0.96); 3/7 (0.77/-)¹⁰; 4a/8a (0.77/0.70) revealed that compounds of the cycloroylenol series 1-4 had the methyl at about δ 0.2 (except 4a/8a) higher field than those of the corresponding compounds 5 - 8 in the cycloartenol series. This difference is generally indicative of euphoid stereochemistry at C-13 and C-14⁶⁾. In agreement with this, the NMR spectra (Table I) of 4a [0.83 (3H, s, C₄ β -Me); 1.02 (3H, s, C₄ α -Me); 0.94 (3H, s, C₁₀-Me); 0.77 (3H, s, C₁₃-Me); 0.90 (3H, s, C₁₄-Me); 0.97 (3H, s, C₂₀-Me); 3.24 (1H, m, 3 α -H); 0.88 (6H, d, J = 7 Hz, C₂₆ and C₂₇ di -Me)] and 4b [0.84 (3H, s, C₄ β -Me), 1.00 (3H, s, C₄ α -Me); 0.91 (3H, s, C₁₀-Me); 0.76 (3H, s, C₁₃-Me); 0.88 (6H, s, C₁₄-Me and C₂₀-Me), 4.5 (1H, m, 3-H), 2.1 (3H, s, C₃-OAc); and 0.89 (6H, d, J = 7 Hz, C₂₆ and C₂₇ di-Me)] are in close agreement with those reported^{8,9)} for these compounds prepared by other methods

The identity of the acetate 4b was further established by the similarity of their properties [Lit.⁷⁾ dihydroeupholacetate: m.p. 123.5-124.5°, (α)_D + 34.5°, derivative 4b, m.p. 124-125°, (α)_D^{30°} + 30.8° (CHCl₃, \underline{c} : 0.190)]. In the case of the alcohol, a difference in m.p. is observed; though the rotations are similar. [Lit.⁷⁾ dihydroeuphol: m.p. 120°, (α)_D + 34°, derivative 4a m.p. 154-156°, (α)_D^{30°} + 32.52°, CHCl₃, \underline{c} : 0.178)]. This comparison of the NMR, m.p. and rotation of the alcohol (4a) and the acetate (4b) established their identity and led uniquely to structure 1a for cycloroylenol.



1a, 13 α -Me, 14 β -Me, 17 β (H), R = H

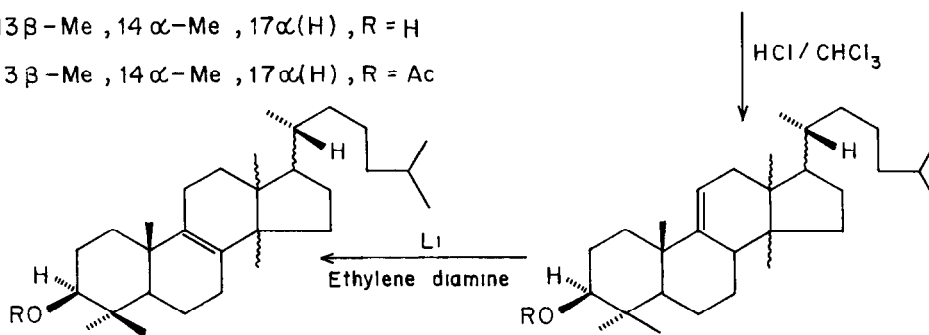
1b, 13 α -Me, 14 β -Me, 17 β (H), R = Ac

5a, 13 β -Me, 14 α -Me, 17 α (H), R = H

5b, 13 β -Me, 14 α -Me, 17 α (H), R = Ac

2, 13 α -Me, 14 β -Me, 17 β (H), R = Ac

6, 13 β -Me, 14 α -Me, 17 α (H), R = Ac



4a, 13 α -Me, 14 β -Me, 17 β (H), R = H

4b, 13 α -Me, 14 β -Me, 17 β (H), R = Ac

8a, 13 β -Me, 14 α -Me, 17 α (H), R = H

8b, 13 β -Me, 14 α -Me, 17 α (H), R = Ac

3, 13 α -Me, 14 β -Me, 17 β (H), R = Ac

7,¹⁰ 13 β -Me, 14 α -Me, 17 α (H), R = Ac

SCHEME - I

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TABLE I. ^1H NMR spectral data of compounds from 1a to 4b (90MHz), CDCl_3
TMS as internal standard

Compound	Proton: <u>4</u> β -Me	<u>4</u> α -Me	<u>10</u> β -Me/ <u>19</u> -CH ₂	<u>13</u> -Me	<u>14</u> -Me	<u>20</u> Me	<u>3</u> α -CH OAc	<u>3</u> α - -CH	<u>24</u>	<u>26</u>	<u>27</u>
Cyclo- roylenol	(<u>1a</u>)	0.81	1.01	AB=0.44 2H, ABdd J=4Hz	0.77	0.88	0.97	3.24, m	-	5.08	1.6 1.69
Cyclo- roylenyl acetate (<u>1b</u>)		0.83	0.97	AB=0.44 2H, ABdd J=4Hz	0.88	0.88	0.88	4.58, m	2.05	5.08	1.6 1.7
Dihydrocyclo- roylenyl acetate (<u>2</u>)		0.81	0.95	AB=0.46 2H, ABdd J=4Hz	0.74	0.87	0.87	4.48, m	2.02	-	0.86 (d, J=7Hz)
$\Delta^{9,11}$ -Dihydro- roylenyl acetate (<u>3</u>)		0.89	1.08	0.98	0.75	0.89	0.89	4.5	2.06	-	0.89
$\Delta^{8,9}$ -Dihydro- euphol (<u>4a</u>)		0.83	1.02	0.94	0.77	0.90	0.97	3.24	-	-	0.88
Reported ⁸⁾		0.83	1.02	0.97	0.77	0.89	0.97	3.24	-	-	0.88
$\Delta^{8,9}$ -Dihydro- eupholacetate (<u>4b</u>)		0.84	1.00	0.91	0.76	0.88	0.88	4.5	2.1	-	0.88
Reported ⁹⁾		0.84	1.00	0.93	0.77	0.89	0.89	-	-	-	0.89

References and Notes

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- 10) Mixture of two products (TLC), obtained.

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