Phytochemistry, Vol. 23, No. 2, pp. 411–413, 1984.
Printed in Great Britain.

0031–9422/84 $3.00 + 0.00

3-EPI-CYCLOLAUDENOL AND KNOWN TRITERPENES FROM *EUPHORBIA CAUDICIFOLIA*

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(*Revised received* 11 *July* 1983)

Key Word Index—*Euphorbia caudicifolia*; Euphorbiaceae; latex; stem; tetracyclic triterpenes; pentacyclic triterpenes; 3-epi-cyclolaudenol; cyclolaudenol; cycloartenol; 3-ketomethylursolate.

Abstract—A new tetracyclic triterpene, 3-epi-cyclolaudenol (24-methyl-9,19-cyclolanost-25-en-3α-ol), cyclolaudenol and cycloartenol were isolated from the ethanolic extract of the latex of *Euphorbia caudicifolia*, and cycloartenol and 3-ketomethylursolate were obtained from the ethanolic extract of the stem of this plant.

INTRODUCTION

Ahmed *et al.* [1] reported the isolation of two diterpenoids, jolkinolide A and caudicifolin, from the root bark of *Euphorbia caudicifolia*. We now report the chemical examination of the latex and stem of *E. caudicifolia*. This investigation revealed the presence in the latex of cyclolaudenol (**1**), cycloartenol (**2**) and a new tetracyclic triterpene named 3-epi-cyclolaudenol (**3**) (24-methyl-9,19-cyclolanost-25-en-3α-ol). The stem contained 3-ketomethylursolate (**4**) and cycloartenol (**2**).

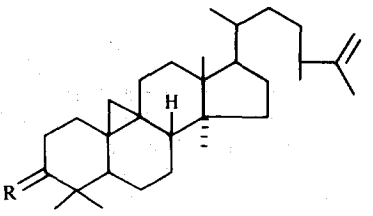
RESULTS AND DISCUSSION

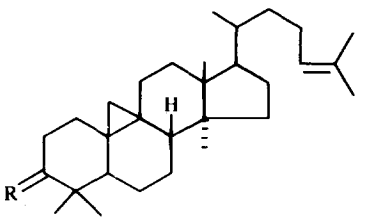
The alcoholic extract of the latex of *E. caudicifolia* furnished a colourless solid (3%) which on repeated crystallization gave cyclolaudenol (**1**). The mass spectrum of **1** with $[M]^+$ at *m/z* 440 ($C_{31}H_{52}O$) had fragment ions (see Experimental which were identical with the reported mass spectrum of cyclolaudenol [2]. The ^1H NMR spectrum of **1** showed signals at δ 0.48 and 0.7 (2H, AB *quartet*, $J = 5$ Hz for the cyclopropane ring), 0.87–1.65 (21H, 7 × Me) and 4.7 (2H, $-C=CH_2$). The IR spectrum of **1** showed bands at 3450 (hydroxyl), 3050 (methylene group of cyclopropane bridge), 1370, 1360 (geminal dimethyls) and 880 cm^{-1} (terminal methylene group). Ozonolysis of **1**-acetate gave formaldehyde and a ketone (**5**). The ^1H NMR spectrum of **5** showed signals at δ 0.43 and 0.65 (2H, AB *quartet*, $J = 5$ Hz for cyclopropane ring), 0.86–1.65 (18H, 6 × Me), 2.01 (3H for –COMe), 1.9 (3H, *s*, –OCOMe) and 4.6 (1H, *t* for 3α-H). The IR spectrum showed bands at 1710 (for –C=O), 1730 (for –COOMe), 3055 (methylene group of cyclopropane ring) and 1370 and 1360 cm^{-1} (geminal dimethyls). Thus compound **1** contained a vinylidene group confirming its identity as cyclolaudenol (**1**). The mother liquor furnished a colourless solid. This was homogeneous as judged by TLC (silica gel G) but the mass spectrum of this material showed to mass peaks at *m/z* 440 ($C_{31}H_{52}O$) and *m/z* 426 ($C_{30}H_{50}O$). TLC examination of the acetate of the above material on ammoniacal silver nitrate impregnated silica gel G plates (10%) showed three spots. They were separated by preparative TLC on ammoniacal silver nitrate impregnated silica gel G plates (10%, 0.1 mm). All the three acetates so obtained were hydrolysed. The compound obtained from the lower spot was identical with cycloartenol (**2**). The mass spectrum of **2** had $[M]^+$ at *m/z* 426 ($C_{30}H_{50}O$) and fragment ions which were identical with those reported in the mass spectrum of cycloartenol [2]. The ^1H NMR spectrum showed signals at δ 0.43 and 0.65 (2H, AB *quartet*, $J = 5$ Hz for cyclopropane ring), 0.87–1.4 (15H, 5 × Me), 1.6 [6H, $-C=C(Me)_2$] and 4.5 ($-CH=C<$). The IR spectrum showed bands at 3400 (OH), 3040 (cyclopropane ring) and 1375, 1360 cm^{-1} (geminal dimethyl). The middle band from TLC was identical with cyclolaudenol with $[M]^+$ at *m/z* 440. The mass spectra of cyclolaudenol (**1**) and the compound from the upper band (compound **3**) were superimposable with $[M]^+$ at *m/z* 440 ($C_{31}H_{52}O$). The ^1H NMR spectrum of **3** showed signals identical to those in the spectrum of cyclolaudenol (**1**). The IR spectrum of **3** differed from cyclolaudenol (**1**) in the fingerprint region. Oxidation of **3** and cyclolaudenol (**1**) furnished the same ketone (**6**) (co-TLC and IR). Hence **3** is concluded to be the 3α-hydroxy isomer of cyclolaudenol (**1**).

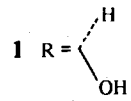
The alcoholic extract of the stem furnished a colourless sticky mass (0.01%). This material was saponified with (10%) alcoholic potassium hydroxide solution and the isolated product subjected to chromatography over alumina to furnish 3-ketomethylursolate (**4**) which had $[M]^+$ at *m/z* 468 ($C_{31}H_{48}O_3$). The major fragments in the mass spectrum of **4** were at *m/z* 262 and 203. The ^1H NMR spectrum of **4** showed signals at δ 5.4 (1H, *s*, –C=CH–), 3.8 (3H, *s*, –COOMe) and 0.9–2.5 (27H, 9 × Me). The IR spectrum of **4** showed bands at 1720 (–C=O), 1590, 1460 (–C=CH), 1380–1370 (geminal dimethyl). Cycloartenol (**2**) was also recovered from the chloroform eluate of the alumina column.

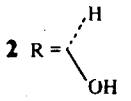
EXPERIMENTAL

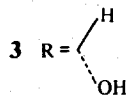
Mps are uncorr. Optical rotations were measured in $CHCl_3$. IR spectra were recorded in KBr and Nujol and ^1H NMR spectra were taken in $CDCl_3$ with TMS as internal standard. Brockmann alumina was used as the adsorbent for column chromatography.





1 R = 

2 R = 

3 R = 

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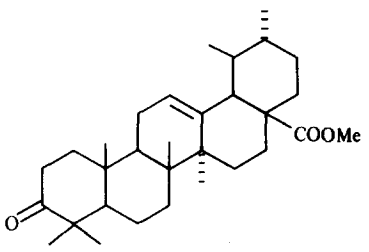

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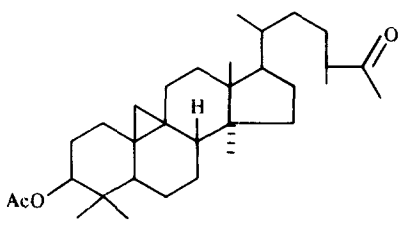

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Extraction and isolation. The latex and stem of *Euphorbia caudicifolia* Hans were collected from around Nalgonda, Andhra Pradesh. The coagulated latex (500 g) of *E. caudicifolia* Hans was refluxed with EtOH (3 × 1 l.) for 12 hr and the mixture filtered hot. The combined extract (3 l.) on removal of the solvent furnished a colourless solid (15 g). This was crystallized 5 × from EtOH, when a pure crystalline solid, homogeneous on silica gel G TLC was obtained (compound **1**). The mother liquor on removal of the solvent furnished a colourless solid, homogeneous on silica gel G TLC. The mass spectrum of this showed two molecular ion peaks at *m/z* 440 and 426. This material was acetylated and examined on ammoniacal $AgNO_3$ impregnated silica gel G plates (10%). It showed three components which were separated by prep. TLC on ammoniacal $AgNO_3$ impregnated silica gel G plates (10%, 0.1 mm). All three acetates were hydrolysed. The compound from the lower band (**2**) crystallized from EtOH as colourless needles. The compound from the middle band was crystallized from MeOH and found to be identical in all respects with compound **1** (TLC and IR). The compound from the upper band (**3**) was purified by crystallization from EtOH.

The dry stems (4 kg) of *E. caudicifolia* were refluxed with EtOH (3 × 3 l.) for 24 hr and the mixture filtered hot. The combined extract on removal of the solvent furnished a colourless pale brown sticky solid. This material (400 mg) on saponification (100 ml 10% alcoholic KOH) furnished a brown solid (300 mg) which showed two spots on silica gel G TLC. It was chromatographed over an alumina (100 g) column and eluted with petrol (5 × 30 ml), C_6H_6 (10 × 30 ml) and finally with $CHCl_3$ (5 × 30 ml). The petrol eluate gave no solid. The C_6H_6 eluate gave compound **4**. The $CHCl_3$ eluate gave a colourless solid identical in all respects (TLC and IR) with compound **2** from the latex.

Compound **1**, mp 125°; $[\alpha]_D$ +46° (*c* 0.928 in $CHCl_3$); MS *m/z*; 440 $[M]^+$ (calc. $C_{31}H_{52}O$); IR ν_{max}^{Nujol} cm^{-1}: 3450 (OH), 3050 (cyclopropane ring), 1370, 1360 (geminal dimethyl), 880 (terminal methylene group). ^1H NMR: δ 0.48 and 0.7 (2H, AB *quartet*, *J* = 5 Hz for cyclopropane ring), 0.87–1.65 (21H, 7 × Me), 4.7 (2H, *s*, >C=CH_2). MS *m/z* (rel. int.): 440 $[M]^+$ (85), 425 $(M-Me]^+$ (42), 422 $[M-H_2O]^+$ (86), 407 (56), 379 (24), 353 (27), 315 (22), 300 (100) and 175 (76). Lit. [3] for cyclolaudenol mp 125°, $[\alpha]_D$ +46°. The acetate (pyridine–Ac_2O) purified by CC and crystallization from EtOH had mp 120°, $[\alpha]_D$ +55° (*c* 0.8950 in $CHCl_3$). Lit. [3] for cyclolaudenyl acetate, mp 132–133°, $[\alpha]_D$ +50°.

Oxidation of compound **1** (pyridine–CrO_3) and purification by CC over alumina and crystallization from EtOH furnished the ketone **6**, mp 110°, $[\alpha]_D$ +16° (*c* 0.6280 in $CHCl_3$). IR ν_{max}^{Nujol} cm^{-1}: 3045 (cyclopropane ring), 1708 (>C=O) and 1370, 1360 (geminal dimethyl). Lit. [3] for cyclolaudenone mp 115°, $[\alpha]_D$ +19°.

Compound **2**, mp 98°, $[M]^+$ at *m/z* 426 (calc. for $C_{30}H_{50}O$), $[\alpha]_D$ +58° (*c* 1.0120 in $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3400 (OH), 1375, 1360 (geminal dimethyl), 3040 (cyclopropane ring). ^1H NMR: δ 0.43 and 0.65 (2H, AB *quartet*, *J* = 5 Hz for cyclopropane ring), 0.87–1.6 (21H, 7 × Me); MS *m/z* (rel. int.): 426 $[M]^+$ (55), 411 $[M-Me]^+$ (53), 408 (72), 393 (60), 365 (24), 339 (25), 315 (9), 286 (57) and 175 (44). Lit. [4] for cycloartenol mp 99°; $[\alpha]_D$ +54°. The acetate (pyridine–Ac_2O) was purified by CC and crystallization from EtOH, mp 129°, $[\alpha]_D$ +55° (*c* 0.9280 in $CHCl_3$), IR ν_{max}^{Nujol} cm^{-1}: 3041, 1730 and 820. Lit. [4] mp 130–132°, $[\alpha]_D$ +59°.

Compound **3**, mp 140°, $[\alpha]_D$ −10° (*c* 0.9324 in $CHCl_3$), MS $[M]^+$ at *m/z* 440 (calc. for $C_{31}H_{52}O$). IR ν_{max}^{Nujol} cm^{-1}: 3430 (OH), 1370, 1360 (geminal dimethyl), 3050 (cyclopropane ring). ^1H NMR: δ 0.48 and 0.7 (2H, AB *quartet*, J = 5 Hz for cyclopropane ring), 0.87–1.65 (21H, 7 × Me), 4.7 (2H, *s*, >C=CH_2). MS *m/z* (rel. int.): 440 $[M]^+$ (85), 425 (42), 422 (86), 407 (56), 379 (24), 353 (27), 315 (22), 300 (100) and 175 (76). The IR spectrum of this compound differed from cyclolaudenol (**1**) only in the fingerprint region.

Oxidation of **3** (pyridine–CrO_3) and purification by CC over alumina followed by crystallization from EtOH furnished the ketone, identical in all respects with **6**, mp 110°, (TLC and IR).

Compound **4**, mp 190°, $[\alpha]_D$ +85° (*c* 0.8242 in pyridine), MS $[M]^+$ at *m/z* 468 (calc. $C_{31}H_{48}O_3$). IR ν_{max}^{Nujol} cm^{-1}: 2900, 1720 (>C=O), 1590, 1460 (–C=CH), 1380, 1370 (geminal dimethyl). ^1H NMR: δ 5.4 (1H, *s*, >C=CH–), 3.8 (3H, *s*, COOMe) and 0.9–2.5 (27H, 9 × Me). MS *m/z* (rel. int.): 468 $[M]^+$ (10), 262 (22), 203 (30). Identical in all respects (IR and TLC) with 3-keto-methylursolate. Lit. [5] 191–192°, $[\alpha]_D$ +83° (pyridine) (authentic sample obtained from the leaves of *D. melanoxylon* [6]).

Acknowledgements—We are greatly indebted to Dr. G. Laxminarayana, Deputy Director, and P. S. Bhasker, Senior Technical Officer of Oil Section RR Labs, Hyderabad, for providing facilities to conduct ozonolysis and separation of constituents; Dr. A. S. R. Anjaneyulu, Department of Chemistry, A. U. Waltair, for ^1H NMR spectra; Dr. N. Ramaiah, Department of Botany, O.U. Hyderabad, for the identification of the plant; and Prof. M. C. Ganorkar, Head, Department of Chemistry, Nizam College, for providing facilities. One of us (Ch.G.) thanks the CSIR, New Delhi for financial assistance.

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