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A TRITERPENOID OF *ANDRACHNE CORDIFOLIA*

K. S. MUKHERJEE, P. BHATTACHARJEE, R. K. MUKHERJEE and P. K. GHOSH*

Department of Chemistry, Visva-Bharati University, Santiniketan 731235, West Bengal, India; *Government Quinine Factory, Mungpoo, Darjeeling, West Bengal, India

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Key Word Index—*Andrachne cordifolia*; Euphorbiaceae; glut-5(10)-en-1β-ol.

Abstract—The petrol extract of the aerial parts and roots of *Andrachne cordifolia* yielded a new triterpene, glut-5(10)-en-1β-ol.

This paper reports the isolation and structural determination of a new pentacyclic triterpene, glut-5(10)-en-1β-ol from the petrol extract of the whole plant of *Andrachne cordifolia* (Euphorbiaceae) [1], on which no phytochemical work seems to have been reported so far.

Glut-5(10)-en-1β-ol, $C_{30}H_{50}O$ (**1**) ($[M]^+$ at *m/z* 426), mp 265–268°, gave a positive Leibermann–Burchardt test for a pentacyclic triterpene. Its IR spectrum exhibited absorption bands at 3495 (hydroxyl) and 1650 cm^{-1} (unsaturation). On acetylation with acetic anhydride and pyridine at room temperature it formed an acetate, $C_{32}H_{52}O_2$ (**2**). The ^1H NMR spectrum of the parent triterpene showed resonances for eight tertiary methyls at δ0.80 (3H, *s*), 0.85 (3H, *s*), 0.95 (3H, *s*), 0.98 (6H, *s*), 1.00 (3H, *s*), 1.10 (3H, *s*), 1.15 (3H, *s*) and one proton multiplet ($W_{1/2}$ = 16 Hz) around δ3.70 assignable to >CH–OH but no signal for unsaturation, thus indicating the tetrasubstituted nature of the unsaturation present in the compound, as also suggested by the IR spectrum.

The mass fragmentation pattern of the compound is similar to that for pentacyclic triterpenes [2] and its mass spectrum records peaks at *m/z* 426 $[M]^+$, 411, 408, 274, 259 and 205 which can be best interpreted in terms of a glut-5(10)-ene skeleton [3]. From the above mass fragmentation pattern it is also evident that the secondary hydroxyl group in the triterpene is present in the A/B ring portion. Further elaboration of the structure (**1**) for the triterpene was possible from its conversion to glut-5(10)-en-1-one (**3**) [3] by chromic acid oxidation.

Conclusive evidence in favour of the equatorial disposition of the C-1 hydroxyl was secured from the ^1H NMR spectrum (90 MHz, $CDCl_3$) of **2**, which disclosed the presence of a multiplet-like single proton signal around δ4.80 with a splitting pattern typical of a β-acetoxyl function [4].

EXPERIMENTAL

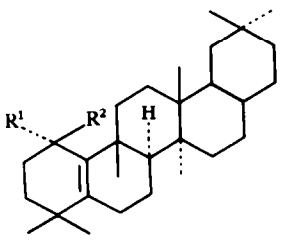
All mps are uncorr. The whole plant of *Andrachne cordifolia* was collected from the Himalayan region and was supplied by United Chemical and Allied Products, Calcutta, India (herbarium sp. No. 906).

Extraction of A. cordifolia. Air-dried powdered whole plant (aerial parts and roots) (1 kg) of *A. cordifolia* was extracted with petrol (60–80°) in a Soxhlet apparatus for 56 hr. The extract was subjected to CC on 200 g silica gel (60–120 mesh). Fractions 70–100 [petrol (60–80°)–C_6H_6 (1:1)] were collected.

Isolation of glut-5(10)-en-1β-ol (**1**). Fractions 70–100 yielded glut-5(10)-en-1β-ol. It crystallized from $CHCl_3$–MeOH (1:1) (yield 0.40 g), mp 265–268°. IR, ^1H NMR (90 MHz, $CDCl_3$) and MS data are described in the text.

Acetylation of **1**. Glut-5(10)-en-1β-ol (0.04 g) was dissolved in 5 ml Ac_2O and 0.5 ml pyridine and the reaction mixture was kept at room temp. for 5 days. The mixture was then poured into cold H_2O and extracted with Et_2O, dried and the solvent evaporated. In this way, the acetate (**2**) was obtained (45 mg), crystallized from EtOAc, mp 235°; IR ν_{max}^{KBr} cm^{-1}: 1735 (acetyl), 1650 (unsaturation); ^1H NMR (90 MHz, $CDCl_3$): δ1.05 (3H, *s*), 1.08 (3H, *s*), 1.00 (6H, *s*), 0.97 (6H, *s*), 0.90 (6H, *s*), 2.00 (3H, *s*, –OAc) 4.80 (1H, *m*, $W_{1/2}$ = 15 Hz, H-1).

Jones oxidation of **1**. Glut-5(10)-en-1β-ol (0.10 g) was dissolved in 30 ml glacial HOAc and to it a soln of chromic acid (0.05 g) in 10 ml glacial HOAc was added. The mixture was refluxed for 2 hr at 50°, cooled and filtered, and the filtrate was acidified with moderately conc HCl in the cold. The ppt. was



1 R^1 = H, R^2 = OH
2 R^1 = H, R^2 = OAc
3 R^1 – R^2 = =O

dissolved in Et_2O, dried and the Et_2O was removed to leave a crude solid which on CC over 50 g silica gel (60–120 mesh) furnished glut-5(10)-en-1-one, $C_{30}H_{48}O$ (3), mp 312°, $[\alpha]_D + 30°$ ($CHCl_3$). It did not respond to a Zimmermann test; its UV, IR, ^1H NMR and MS data were similar to those in the lit. [3].

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REFERENCES

1. Chopra, R. N., Nayar, S. L. and Chopra, I. C. (1956) *Glossary of Indian Medicinal Plants*, p. 18. Council of Scientific and Industrial Research, New Delhi.
2. Budzikiewicz, H., Wilson, J. N. and Djerassi, C. (1963) *J. Am. Chem. Soc.* **85**, 3688.
3. Anjeneyulu, A. S. R., Row, R., Subrahmaynyam, C. and Murty, K. S. (1973) *Tetrahedron* **29**, 3909.
4. Bhacca, N. S. and Williamson, D. H. (1964) *Application of NMR Spectroscopy in Organic Chemistry*, p. 78. Holden-Day, San Francisco.

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3-ACETYLMASLINIC ACID FROM THE ROOT BARK OF *TERMINALIA ALATA**

A. S. R. ANJANEYULU,† A. V. RAGHAVA REDDY,† GOPAL R. MALLAVARAPU‡ and R. S. CHANDRASEKHARA‡

†School of Chemistry, Andhra University, Waltair 530003, India; ‡Central Institute of Medicinal and Aromatic Plants, Regional Centre, Bangalore 560037, India

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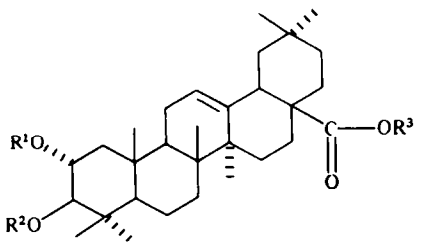
Key Word Index—*Terminalia alata*; Combretaceae; triterpenoids; 3-acetylmaslinic acid.

Abstract—A new triterpene acid, 3-acetylmaslinic acid, has been isolated from the root bark of *Terminalia alata* together with oleanolic acid, arjunic acid, arjunolic acid and arjunetin.

The isolation of triterpenoids from the heartwood of *Terminalia alata* Heyne *ex* Roth (syn. *T. tomentosa* W. & A.) was reported recently [1, 2]. Continuing our studies on the chemical constituents of the genus *Terminalia*, we report here the isolation of a new triterpene acid, identified as 3-acetylmaslinic acid, from the root bark of *T. alata* together with the known compounds oleanolic acid, arjunic acid, arjunolic acid and arjunetin.

Extraction of the ground root bark with $CHCl_3$ and EtOAc afforded a mixture of triterpenoids. Separation by repeated column chromatography and preparative TLC over silica gel led to the isolation of the above known triterpene acids and the new acid TARB-2. The compound TARB-2, mp 192–195°, $[\alpha]_D + 32°$, analysed for $C_{32}H_{50}O_5$ and gave a positive Liebermann–Burchard test and yellow colour with tetranitromethane. Its IR spectrum showed the presence of hydroxyl (3500 cm^{-1}), ester carbonyl (1740 cm^{-1}) and carboxyl (1690 cm^{-1}) groups. The ^1H NMR spectrum showed the resonances for seven tertiary methyls, one acetate and olefinic groups. In addition, it showed the presence of CHOH with a signal at δ3.29 (*m*) and a CHOAc signal at 4.68 (*d*, J = 12 Hz). The large coupling constant indicated a diaxial relation; therefore the hydroxyl and acetoxyl groups are in diequatorial orientation. Acetylation with acetic anhydride and pyridine gave diacetylmaslinic acid (**1b**), which on treatment with diazomethane afforded diacetylmethyl



1 $R^1 = R^2 = R^3 = H$
1a $R^1 = R^3 = H$; $R^2 = Ac$
1b $R^1 = R^2 = Ac$; $R^3 = H$
1c $R^1 = R^2 = Ac$; $R^3 = Me$

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