

A new triterpenic constituent from *Andrachne cordifolia*

K. S. Mukherjee* and B. Mukhopadhyay

Department of Chemistry, Visva-Bharati University, Santiniketan-731 235, India

E-mail : bodhitukun@yahoo.co.in

Manuscript received 3 November 2004, revised 26 May 2005, accepted 2 July 2005

The petrol (60–80°) extract of the whole plant (aerial parts and roots) of *Andrachne cordifolia*. Muel-Arg yielded a new pentacyclic triterpene, glut-5(10)-en-3 β -ol.

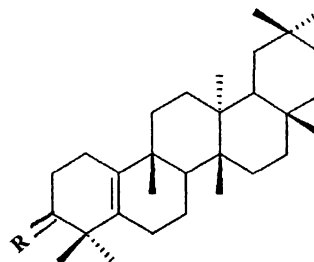
In our previous communication¹, we reported the isolation and characterization of two triterpenoid constituents from the petrol (60–80°) extract of *Andrachne cordifolia*. We now report the isolation and structure elucidation of a new triterpene from the same plant.

The concentrated petrol (60–80°) extract of the whole plant (aerial parts and roots) of *A. cordifolia* obtained by following the same procedure as in our previous communication on chromatographic resolution over silica gel (60–120 mesh) afforded a white solid, C₃₀H₅₀O (M⁺, *m/z* 426) m.p. 230–232°. It responded positively to Lieberman-Burchard test for pentacyclic triterpene. Its IR spectrum recorded bands at 3490 (OH) and 1650 cm⁻¹ (unsaturation). The ¹H NMR (90 MHz, CDCl₃) spectrum of the triterpene showed signals for eight tertiary C-methyls at δ 0.82 (3H, s), 0.85 (3H, s), 0.95 (3H, s), 0.98 (3H, s), 1.00 (3H, s), 1.10 (3H, s), 1.15 (6H, s) and one proton multiplet around δ 3.70 (*w*_{1/2} 16 Hz) assignable to carbinol methine proton but no signal for unsaturation, thus indicating the tetra substituted nature of the unsaturation as also suggested by the IR spectrum. The compound readily forms an acetate, C₃₂H₅₂O₂ (M⁺, *m/z* 468) (2), m.p. 210–212° on treatment with acetic anhydride in pyridine. The mass fragmentation pattern of the parent compound is similar to that for pentacyclic triterpene² 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 skeleton³. From mass fragmentation pattern it is also evident that the secondary hydroxyl in the triterpene is present in A/B ring portions.

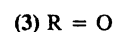
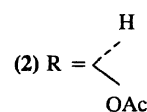
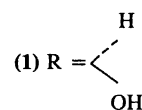
On oxidation with chromic acid, the parent triterpene yielded a ketone, C₃₀H₄₈O, m.p. 250–253°; ν_{\max} (KBr) 1730, 1650 cm⁻¹ which was found to be identical with glut-5(10)-en-3-one (3)¹ by direct comparison of physical and spectral data with the authentic sample (m.m.p., Co-

IR and Co-TLC). This settles the nature of the skeleton as well as the location of hydroxyl function at C-3 position.

Conclusive evidence in favour of the equatorial disposition of C-3 hydroxyl was secured from the ¹H NMR spectrum of (90 MHz, CDCl₃) of the acetate (2) which disclosed the presence of a multiplet-like one proton signal around δ 4.82 (*w*_{1/2} 15 Hz) with splitting pattern typical of a β -acetoxyl function⁴. These led us to formulate this new triterpene as glut-5(10)-en-3 β -ol (1).



(1)



The structure of the compound 1 also received support from ¹³C NMR data as below, which are comparable to those compounds having similar skeleton⁵.

c(δ) : 1 (39.00), 2 (15.00), 3 (80.00), 4 (46.00), 5 (143.20), 6 (19.20), 7 (33.00), 8 (40.50), 9 (53.00), 10

(142.80), 11 (23.80), 12 (24.50), 13 (37.00), 14 (42.80), 15 (28.30), 16 (24.20), 17 (45.00), 18 (42.50), 19 (45.80), 20 (32.50), 21 (34.20), 22 (33.30), 23 (26.00), 24 (22.50), 25 (18.20), 26 (18.00), 27 (19.50), 28 (28.70), 29 (32.00), 30 (24.00).

Experimental

All m.p. are uncorrected. The whole plant of *Andrachne cordifolia* was supplied by M/s. United Chemical and Allied Products, Kolkata, India.

Air dried powdered whole plant (1 kg) of *A. cordifolia* was extracted with petrol (60–80°) in a soxhlet apparatus for 56 h. The extract was concentrated under pressure and then subjected to CC on silica gel (60–120 mesh, 200 g). The petrol (60–80°) : benzene (1 : 1) eluent yielded the compound **1** (0.5 g) m.p. 230–232°. IR ¹H NMR, ¹³C NMR and EIMS are described in the text. It may be mentioned in this connection that the triterpene is expected to have property of curing eye-sore⁶.

Acetylation of triterpene 1 : The triterpene (**1**, 0.05 g) was dissolved in 5 ml acetic anhydride and 2 ml pyridine. The reaction was allowed to stand for four days at room temperature. The reaction was then poured into ice cold water, extracted with ether and dried when an acetate (**2**), 0.06 g, m.p. 210–212° was obtained.

Jones oxidation of triterpene 1 : The triterpene **1** (0.2 g) was dissolved in 30 ml acetic HOAc and to it a solution of chromic acid (0.5 g) in 15 ml glacial HOAc was added. The mixture was refluxed for 2 h at 50°, cooled, filtered and the filtrate was acidified with moderately conc. HCl in the cold. The ppt was dissolved in ether, dried

and evaporated. The crude solid on chromatography over silica gel (60–120 mesh, 50 g) furnished glut-5(10)-en-3-one (**3**, 0.1 g), C₃₀H₄₈O [M⁺], m/z 424, m.p. 250–253°, ν_{\max} (KBr), 1700, 1650 cm⁻¹; ¹H NMR (90 MHz, CDCl₃) δ 0.81 (3H, s), 0.84 (3H, s), 0.93 (3H, s), 0.95 (6H, s), 1.00 (3H, s), 1.15 (3H, s) for eight tertiary methyls, δ 2.38 (2H, m) ascribed to keto methylene protons.

Acknowledgement

Authors are thankful to R.S.I.C., I.I.T., Chennai and R.S.I.C., Lucknow for spectral measurements. They are also grateful to M/s. United Chemical and Allied Products, Kolkata for supplying plant materials and Visva-Bharati University for financial assistance.

References

1. K. S. Mukherjee and P. Bhattacharya, *Phytochemistry*, 1986, **25**, 2669; 1987, **26**, 1539.
2. H. Budzikiwicz, J. M. Wilson and C. Djerassi, *J. Am. Chem. Soc.*, 1963, **85**, 3688.
3. A. S. R. Anjaneyulu, Ramchandra Rao, C. Subrahmanyam and K. S. Murty, *Tetrahedron*, 1973, **29**, 3909.
4. N. S. Bhacca and D. H. Williamson, "Application of NMR Spectroscopy in Organic Chemistry", Holden-Day, San Francisco, 1964, p. 78.
5. H. Buddeck, M. H. A. Elgamol, G. S. Ricca, B. Danielli and G. Palmisano, *Org. Magn. Reson.*, 1978, **11**, 130; T. K. Chen, D. C. Ales, N. C. Baewziger and D. F. Weimer, *J. Org. Chem.*, 1983, **48**, 3525; G. S. Ricca, B. Danielli, G. Palmisano, G. Duddeck and M. H. A. Elgamol, *Org. Magn. Reson.*, 1978, **11**, 163.
6. "Medicinal Plants of India", ICMR, New Delhi, 1976, p. 64.