

Triterpene from *Adiantum lunulactum*

K. S. Mukherjee*, G. Brahmachari, D. Chatterjee and P. Mukherjee

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

Manuscript received 19 January 2000, revised 21 December 2000, accepted 26 December 2000

The petrol extract of the whole plants of *Adiantum lunulactum* has yielded a new hopane triterpene, 3 β -acetoxy-21 α -H-hop-22(29)ene.

Adiantum lunulactum Burm. (syn. *Adiantum philippense* Linn.) (Adiantaceae)¹, commonly known as walking maidenhair fern, is used widely as traditional medicine in the treatment of various diseases¹. No chemical examination has been carried out on this plant. The present communication reports the isolation and characterization of a new hopane triterpene from the petrol extract of *A. lunulactum*.

3 β -Acetoxy-21 α -H-hop-22(29)ene (1), C₃₂H₅₂O₂ ([M]⁺ at *m/z* 468), [α]_D + 25° (CHCl₃), responded positively to Liebermann-Burchardt test for triterpene. Its IR spectrum showed bands at 1700 (ester C=O) and 1645 cm⁻¹ (unsaturation). The ¹H NMR spectrum of the triterpene displayed signals for (i) seven tertiary methyls at δ 0.68 (3H, s), 0.75 (3H, s), 0.91 (3H, s), 0.98 (3H, s), 1.2 (6H, s) and 1.70 (3H, s, methyl protons of isopropenyl moiety), (ii) two vinylic protons at δ 4.72 (2H, m), (iii) a three-proton singlet at δ 2.05 for the methyl group of an acetoxy function and (iv) one proton multiplet at δ 4.50 (br, half-band width 15 Hz) assignable to the carbonyl proton.

The mass spectral fragmentation of the compound is closely similar to that of hopane type triterpene² showing peaks at *m/z* 468 [M]⁺, 409 [M-OAc]⁺, 408 [M-AcOH]⁺, 250 (retro-Diels-Alder fragmentation around ring C), 249 [250-H]⁺, 218 (retro-Diels-Alder fragmented ion peak), 190 [250-AcOH]⁺, 189 [249-AcOH]⁺, 262, 189 (cleavage around ring C), 247 [262-CH₃]⁺, 202 [262-AcOH]⁺, 187 [202-CH₃]⁺, 174 [189-CH₃]⁺ and 148 [189-C(CH₃)=CH₂]⁺. Thus it is evident that the acetoxy group is in the A/B ring system. Again, the triterpene on hydrolysis with alcoholic KOH furnished a compound, C₃₀H₅₀O (2), which on oxidation with chromium trioxide-pyridine yielded compound 3, identified as moretenone³ by comparison of physical constants, spectral and m.m.p. data with the authentic sample⁴, establishing that the hydroxyl group is located at C-3 of 2. Further, appearance of C₃-H proton at δ 3.60 (m, half-band width 16 Hz) in the ¹H NMR spectrum of the hydrolysate 2 and at 4.50 (m, half-band width 15 Hz) in the parent compound indicates the equatorial disposition of the acetoxy group⁵. These led us to formulate this

triterpene as 3 β -acetoxy-21 α -H-hop-22(29)ene (1). The structure of the compound 1 also received support from its ¹³C NMR data (Table 1) which are comparable to those compounds having similar type of skeleton⁶.

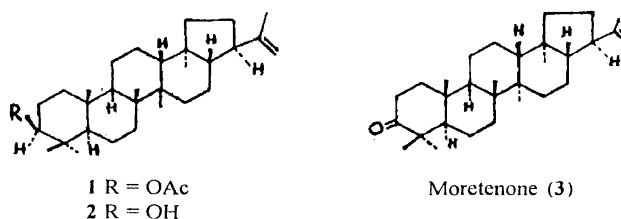


Table 1. ¹³C NMR chemical shifts of compound 1

| C | δ | C | δ |
|----|----------|-----|-----------------------|
| 1 | 40.2 | 17 | 53.2 |
| 2 | 23.4 | 18 | 43.9 |
| 3 | 81.1 | 19 | 39.9 |
| 4 | 37.5 | 20 | 23.9 |
| 5 | 56.2 | 21 | 44.2 |
| 6 | 18.7 | 22 | 148.8 |
| 7 | 32.9 | 23 | 33.4 |
| 8 | 41.8 | 24 | 16.4 |
| 9 | 50.3 | 25 | 15.9 |
| 10 | 37.5 | 26 | 16.8 |
| 11 | 21.0 | 27 | 16.7 |
| 12 | 22.8 | 28 | 15.2 |
| 13 | 48.5 | 29 | 110.7 |
| 14 | 42.2 | 30 | 25.6 |
| 15 | 32.6 | OAc | 21.9 (Me); 170.1 (CO) |
| 16 | 21.5 | | |

Experimental

All m.ps. are uncorrected. Whole plants of *A. lunulactum* were supplied by the United Chemical and Allied Products, Calcutta, India. A specimen of the plant is preserved in the Natural Products Laboratory of Visva-Bharati University.

Air-dried defatted powdered whole plant (1.5 kg) of *A. lunulactum* was extracted with petrol (b.p. 60–80°) in a

Soxhlet apparatus for 56 h. The extract was concentrated under reduced pressure and then subjected to CC on silica gel (60–200 mesh; 200 g). The petrol–benzene (1 : 1) eluent afforded compound **1** (1.45 g), m.p. 283–284°; UV, IR, ¹H NMR (90 MHz, CDCl₃), ¹³C NMR (100 MHz, CDCl₃) and mass spectral data are discussed in the text.

Hydrolysis of triterpene 1 : The triterpene (**1**; 0.5 g) was refluxed with 20% ethanolic KOH (10 ml) for 8 h, then the solvent removed, H₂O added and the mixture filtered. The residue on repeated CC over silica gel (50 g) furnished hydrolysate (**2**; 0.056 g), m.p. 235–237°, C₃₀H₅₀O, [α]_D + 28° (CHCl₃), [M]⁺ *m/z* 426; ν_{max} (KBr) 3450 (OH), 1642 cm⁻¹ (unsatn.); ¹H NMR (90 MHz, CDCl₃) δ 0.68 (3H, s), 0.74 (3H, s), 0.90 (3H, s), 0.99 (3H, s), 1.20 (6H, s), 1.73 (3H, s) for seven tertiary methyls, 4.74 (2H, m, vinylic protons), 3.60 (m, half-band width 16 Hz) assignable to carbinol methine proton at C₃.

Oxidation of hydrolysate 2 : CrO₃ (3 g) was added to a stirred solution of dry pyridine (4.6 g) in dry dichloromethane (75 ml). After stirring the whole contents, the hydrolysate (**2**; 0.2 g) was added as a solution in a small volume of dichloromethane. The reaction mixture was stirred for about 15 min, then filtered and the filtrate was concentrated in vacuo, taken up in ether, filtered to remove chromium salts, washed with dilute aq. NaOH and saturated brine and dried over magnesium sulfate. Evaporation of the solvent at reduced pressure afforded moretenone **3** (0.102 g), m. p. 206–207°, C₃₀H₄₈O, [α]_D + 54°, [M]⁺ *m/z* 424; ν_{max} (KBr) 1730 (C=O), 1645 cm⁻¹ (unsatn.); ¹H NMR (90 MHz, CDCl₃) δ 0.69 (3H, s), 0.75 (3H, s), 0.92 (3H, s), 0.96 (3H, s), 1.25

(6H, s), 1.69 (3H, s) for seven tertiary methyls, 4.71 (2H, m, vinylic protons), 2.30 (2H, m) assignable to ketomethylene protons of COCH₂ group.

Acknowledgement

The authors are grateful to R.S.I.C., I.I.T. (Chennai) and R.S.I.C., C.D.R.I. (Lucknow) for spectral measurements. They are also grateful to the United Chemical and Allied Products (Calcutta) for supplying the plant materials and to Dr. H. R. Chowdhury and Dr. S. Mondal for the identification of the plant.

References

1. "The Useful Plants of India", ed.-in-chief S. P. Ambasta, PID, C.S.I.R., New Delhi, 1986; R. N. Chopra, S. L. Nayar and I. C. Chopra, "Glossary of Indian Medicinal Plants", C.S.I.R., New Delhi, 1956.
2. R. E. Corbett and H. Young, *J. Chem. Soc. (C)*, 1966, 1556, 1564.
3. M. N. Galbraith, C. J. Miller, J. W. L. Rowson, E. Ritchie, J. S. Shannon and W. C. Taylor, *Asut. J. Chem.*, 1965, **18**, 226.
4. K. S. Mukherjee, G. Brahmachari and T. K. Manna, *J. Indian Chem. Soc.*, 1997, **74**, 738.
5. N. S. Bhacca and D. H. Williams, "Application of NMR Spectroscopy in Organic Chemistry", Holden-Day, London, 1964; M. Sharma, R. E. Glick and R. O. Mumma, *J. Org. Chem.*, 1962, **27**, 4512; P. Chakraborti, *Tetrahedron*, 1969, **25**, 3301; M. Hamburger, G. Dudan, A. G. R. Nair, R. Jayprakasam and K. Hostettmann, *Phytochemistry*, 1989, **28**, 1767.
6. A. L. Wilkins, P. W. Birr and P. M. Jager, *Magn. Reson. Chem.*, 1987, **25**, 503; K. Shiojima and H. Ageta, *Chem. Pharm. Bull.*, 1990, **38**, 347.