Note

A new triterpene from *Adiantum lunulatum* Burm.

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From the petrol extract of the whole plants of *Adiantum lunulatum* Burm. (Adiantaceae) a new triterpene characterized as 3β-acetoxy-6α-hydroxy-hop-15,17(21)-dien e I has been isolated and its structure elucidated with the help of spectral as well as chemical studies.

*Adiantum lunulatum* Burm, syn. *Adiantum Philip­pense* Linn. (Adiantaceae), commonly known as walking maidenhair fern, is highly rich in medicinal efficacies and used in the treatment of various diseases among the local and tribal people traditionally. The present communication deals with the isolation and characterization of a new hopane triterpene I from the petrol extract of this plant.

**Results and Discussion**

The compound I, C₃₂H₅₀O₃ ([MI] at m/z 482), gave positive Liebermann-Burchardt test and a reddish-brown colour with tetrinitromethane confirming it to be an unsaturated triterpene. Its UV(methanol) and IR spectral properties are indicative of a heteroannular diene chromophore similar to those of either olean-11:12, 13:18-dienes or hop-15, 17(21)-dienes. That the compound I is a hopane type triterpene having 15, 17(21)-diene system was clear from its IR, ¹H NMR, EIMS and ¹³C NMR spectral studies as well as its conversion experiments. The ¹H NMR spectrum of the triterpene I displayed signals for six tertiary methyl groups at δ0.8-3.6(H, s), 0.92(3H, s), 0.94(3H, s), 1.02(3H, s), 1.11(3H, s) and 1.32(3H, s); an isopropyl group at δ1.96 (3H, d, J=6Hz), 0.98 (3H, d, J=6Hz) and 2.70(1H, m); an acetoxy group at δ2.1(3H, s); a carbinolmethine proton at δ3.98 (1H, br.multiplet, half band-width 16Hz); an acetoxy bearing methine proton at δ4.1 (1H, br.multiplet, half band-width 15Hz) and a heteroannular diene at δ5.7(1H, d, J=10Hz), 6.5(1H, d, J=10Hz) and 2.3(2H, m) in the molecule. Further support in favour of the presence of the above functionalities as well as the structural pattern of the triterpene I were received from its ¹³C NMR spectral analyses.


The triterpene I on hydrolysis with alcoholic KOH furnished a compound, C₃₀H₄₈O₂(2), which on acetylation formed a diacetate derivative 3 and on benzoylation gave a dibenzoate derivative 4, thereby suggesting the presence of two hydroxyl functions in the resulting hydrolysate 2. The hydrolysate 2 was found to be identical with 3β, 6α-dihydroxy-hop-15,17(21)-dien e (mollugogenol B) by comparison of its physical constants and spectral properties (UV, IR, ¹H NMR, EIMS and ¹³C NMR spectral data) along with those of its diacetate 3 and dibenzoate 4 derivatives with those of the reported values for
mollugogenol B and its diacetate and dibenzoate derivatives. Consequently, C₃ and C₆ positions in the parent molecule are shared by the acetoxy and hydroxy functions. Appearance of C₃-H and C₆-H protons respectively at δ 4.3(1H, m, H-3α) and 4.0(1H, m, H-6α) in the ¹H NMR spectrum of hydrolysate 2 and respectively at δ 4.1(1H, m, H-3α) and 3.98(1H, m, H-6α) in the ¹H NMR spectrum of the parent triterpene 1, unequivocally disclosed the positions and stereochemical configurations of the acetoxy and hydroxy groups in the triterpene 1—the acetoxy function is located at C₅ and it is equatorial and having α orientation. Thus, the aforediscussed observations led us to formulate this triterpene as 3β-acetoxy, 6α-hydroxy-hop-15, 27(21)-dien-20-one 1. Finally, the structure has been further confirmed by analyzing its ¹³C NMR spectral data compared with those of other compounds having similar type of skeleton.

Experimental Section

All mps are uncorrected. A. lunulatum plant materials were supplied by the M/S United Chemical and Allied Products, Kolkata (WB), India and taxonomically authenticated by a taxonomist of the Botany Department of this University. A herbarium specimen is deposited in the Natural Products Laboratory, Department of Chemistry, Visva-Bharati University, Santiniketan (WB).

Extraction and isolation of triterpene 1. Air-dried and powdered whole plants (1.5 kg) of A. lunulatum were Soxhlet extracted with petrol (60-80°C). The extract was concentrated under reduced pressure and the crude product (42g) then subjected to chromatographic separation on Si-gel (60-80°C).

Acetylation of compound 2. The dihydroxy compound (2; 200mg) was dissolved in pyridine (5mL) and to this Ac₂O (10mL) was added and the mixture heated at 100°C in a water-bath for 12 hr. After usual work-up colourless crystals of 3, C₃₆H₄₇O₃₆, mp 194°-196°C, [M]⁺ at m/z 524 were obtained. UV(methanol): λ_{max} (logε) at 262(4.01), 250(4.22) & 243(4.11) nm; IR(KBr): 3450, 3010, 2930 cm⁻¹; ElMS: m/z (rel. int.): 440(M⁺, 4), 425(4.8), 422(3.8), 407(2.5), 404(2.1), 397(3.5), 389(3.1), 232(2.7), 222(3.9), 218(10.1), 217(9.2), 204(3.2), 203(3.1), 202(2.2), 200(6.5), 189(7.1), 186(100), 174(1.5); ¹H NMR (400MHz, CDCl₃): δ 0.84(3H, s), 0.92(3H, s), 0.94(3H, s), 1.02(3H, s), 1.11(3H, s) and 1.29(3H, s) for six tertiary methyls; δ 0.96 (3H, d, J = 6 Hz), 0.98 (3H, d, J=6Hz) and 2.70(1H, m) for an isopropyl moiety; δ 3.20(1H, m, H-20), 4.01(1H, m, H-20), 5.58(1H, m, J=10Hz, H-15), 6.21(1H, m, J=10Hz, H-16), 2.18 (2H, m, H-20); ¹³C NMR(100MHz, CDCl₃): δ 15.4(C-25), 16.3(C-24), 17.4(C-27), 18.6(C-26), 19.8(C-28), 20.8(C-30), 21.3(C-29), 21.8(C-11), 22.2(C-12), 24.8(C-2), 26.5(C-22), 27.8(C-20), 32.6(C-23), 38.5(C-1), 39.3(C-10), 39.7(C-7), 40.7(C-4), 41.6(C-8), 45.2(C-19), 45.8(C-14), 46.2(C-13), 49.8(C-18), 50.1(C-9), 56.1(C-5), 68.1(C-6), 80.9(C-3), 119.7(C-15), 133.9(C-16), 138.5(C-17), 140.3(C-21), 170.1 & 21.2(3b-OAc); ElMS: m/z(rel. int.) 482(M⁺, 9.1), 481(31.8), 467(5.4), 439(3.4), 423(2.8), 422(3.9), 404(2.5), 389(3.4), 361(2.2), 278(10.5), 265(11.2), 264(8.5), 260(2.4), 218(10.8), 217(9.7), 204(3.4), 203(3.2), 189(7.2), 186(100), 161(4.2); ¹H NMR (400MHz, CDCl₃) spectral data are described in the text.

Saponification of triterpene 1 to dihydroxy derivative 2. The compound (1.4g) was refluxed with 20% ethanolic KOH (10mL) for 8 hr, the solvent removed, H₂O added and filtered. The residue on column chromatography (repeated twice) over Si-gel(50g) furnished dihydroxy compound (2; 0.96g), white crystals, C₃₆H₄₇O₃₆, m.p. 223°-225°C, [α]D +91° (CHCl₃), [M]⁺ at m/z 440; UV(methanol): λ_{max} (logε) at 261(4.0), 250(4.2), 244(4.1) nm; IR(KBr): 3450, 3010, 2930, 2820 and 1700 (unsymmetrically trisubstituted double bond), 1370, 1380, 1160cm⁻¹; ElMS m/z (rel. int.): 440(M⁺, 4), 425(4.8), 422(3.8), 407(2.5), 404(2.1), 397(3.5), 389(3.1), 232(2.7), 222(3.9), 218(10.1), 217(9.2), 204(3.2), 203(3.1), 202(2.2), 200(6.5), 189(7.1), 186(100), 174(1.5); ¹H NMR (400MHz, CDCl₃): δ 0.84(3H, s), 0.92(3H, s), 0.94(3H, s), 1.02(3H, s), 1.11(3H, s) and 1.29(3H, s) for six tertiary methyls; δ 0.96 (3H, d, J = 6 Hz), 0.98 (3H, d, J=6Hz) and 2.70(1H, m) for an isopropyl moiety; δ 3.20(1H, m, H-20), 4.01(1H, m, H-20), 5.58(1H, m, J=10Hz, H-15), 6.21(1H, m, J=10Hz, H-16), 2.18 (2H, m, H-20); ¹³C NMR(100MHz, CDCl₃): δ 15.4(C-25), 16.3(C-24), 17.4(C-27), 18.6(C-26), 19.8(C-28), 20.8(C-30), 21.3(C-29), 21.8(C-11), 22.2(C-12), 24.1(C-2), 26.3(C-22), 27.9(C-20), 33.1(C-23), 38.2(C-2), 39.2(C-10), 39.9(C-7), 37.8(C-4), 41.9(C-8), 45.3(C-19), 45.6(C-14), 46.6(C-13), 49.7(C-18), 50.2(C-9), 60.7(C-5), 68.8(C-6), 78.6(C-3), 119.6(C-15), 133.5(C-16), 138.5(C-17), 140.7(C-21).
Benzoylation of compound 2. The dihydroxy compound (2; 200mg) was dissolved in pyridine (8mL), redistilled benzoyl chloride (5mL) was added and the mixture heated at 100°C in a water-bath for 12 hr. After usual work-up colourless crystals of dibenzoate derivative 4, C_{44}H_{56}O_{4}, mp 221°-24°C, [M]+ m/z 648 were obtained. UV(methanol): λ_{max} (log ε) at 260(4.01), 252(4.2), 242(4.1)&230(4.07)nm; IR (KBr): 3080, 3010, 2930, 1720, 1726 (2 x C\textsubscript{6}H\textsubscript{5}COO), 1645, 1600, 1580, 1500, 1380, 1370, 1250, 845 cm\textsuperscript{-1}.

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