CHEMICAL INVESTIGATION OF THE STEM BARK OF APHANAMIXIS POLYSTACHYA

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The plant Aphanaemixis polystachya (syn. Amoa rohitukha) is a medicinal plant employed in our indigenous system of medicine. This communication records the isolation and characterization of three compounds—A, B and C. The compounds A and B were identified as β-sitosterol and stigmasterol by direct comparison with their authentic specimens. Chemical investigation so far on the stem bark of A. polystachya has not been reported earlier but the seed of this plant was investigated by Chatterjee et al. and was found to contain aphanaemixin.

Air-dried and powdered stem bark (10 kg) of A. polystachya, procured from the United Chemicals and Allied Products, Calcutta, was exhaustively extracted thrice to rectified spirit under reflux for 30 days. The total spirit extract (30 l) was concentrated (500 ml) under reduced pressure and segregated into water soluble and insoluble fractions. The water insoluble material was extracted with pet ether (b.p. 60–80°C). The pet ether extract gave a mixture of three compounds (on TLC) which were separated on Al₂O₃ column to yield compound-A (800 mg, hexane: pet ether, 9:1); B (750 mg, hexane: pet ether, 7:3) and C (2.5 g, pet ether). Compounds A and B were found to be identical with β-sitosterol and stigmasterol with their authentic specimens (m.p., m.m.p. and Co-TLC).

**Compound-C:** M.P. 138–40°C, (α)²D +4.2° (CHCl₃), C₄₁H₆₈O₁₀. It gave characteristic reactions of a saponin. Acid hydrolysis (7% H₂SO₄) of the saponin afforded a genin, Ia and L-rhamnose and D-xylene (Co-PC).

The genin, m.p. 112–13°C, (α)²D +53° (CHCl₃), C₃₀H₅₀O₂ (M⁺ 442), gave all the positive tests for a terpene [8] and decolourized bromine water in CCl₄; UV: 170 nm, (ε 212)° (disubstituted double bond); IR (principal bands): hydroxyl [10] (3580 and 3453), vinylic (3050 and 1639) probably as C=CH₂ (880 cm⁻¹); PMR (CDCl₃, 90 MHz, Me₂Si δ): 0.76 (4x-Me), 0.85 (4β-Me), 0.87 (14α-Me), 0.98 (8β-Me), 0.99 (10β-Me), 1.25 and 1.32 (25-Me₂), 2.75 (symmetrical t, 24-H), 3.25 (m, 3x-H, a carbon atom bearing oxygen) and 4.75 (bs, 21-CH₃). The low field absorptions of 2 x Me (1.25 and 1.35) could be accounted for the presence of one oxygen atom as a cyclic ether in the form of a triplet as in dammarane derivatives. The mass spectrum of Ia showed the fragments at m/e 442 (M⁺), 427 (M⁺-Me), 424 (M⁺-H₂O), 409[M⁺-(Me+H₂O)], 343 (M⁺-C₆H₁₁O), 344 (M⁺-C₆H₁₅O), 317 (M⁺-C₆H₁₅O), 318 (M⁺-C₆H₁₄O), 189 and 187.

Ia formed an acetate (Ac₂O/py), lb at room temperature (30 hr), m.p. 160–62°C, C₃₃H₅₂O₅ (M⁺ 484) (Found: C, 79.32; H, 10.75; C₃₃H₅₂O₅ reqd., C, 79.34; H, 10.74%); (α)²D +68° (CHCl₃); IR: 1740 cm⁻¹; PMR (δ): 2.01 (acetate methyl), 4.50 (3α-H) and other usual signals.

Reduction of Ia with Pd-C gave II, m.p. 112–15°C, C₃₀H₅₂O₂ (M⁺ 444) (Found: C, 81.00; H, 11.70; C₃₀H₅₂O₂ reqd., C, 81.08; H, 11.71%); (α)²D +6° (CHCl₃); PMR (δ): 8 x Me (0.76, 0.84, 0.85, 0.97, 0.98, 1.00, 1.27 and 1.28) and a symmetrical triplet (2.65 m, 24-H). Ia with LAH treatment yielded III, m.p. 142–44°C, C₃₀H₅₂O₂ (M⁺ 444) (Found: C, 81.02; H, 11.69; C₃₀H₅₂O₂ reqd., C, 81.08; H, 11.71%); (α)²D +50°; IR: 3500 (OH), 3055, 1640 and 887 (vinyllic) cm⁻¹; PMR (δ): 0.77, 0.84, 0.87, 0.95, 0.98, 1.20 and 1.28, 7 x Me; 4.70, vinyllic-H and 3.22, bm, 3x-H.

The acetylation (Ac₂O/py) of III at room temperature afforded IIIa, m.p. 138–39°C, C₃₂H₅₄O₃ (M⁺ 486) (Found, C, 79.00; H, 11.00; C₃₂H₅₄O₃ reqd., C, 79.01; H, 11.11%); (α)²D +70° (CHCl₃); IR: 3500 (OH) and 1735 (acetate carbonyl); PMR (δ): 2.00 (s, 1 x OAc) while the acetylation (Ac₂O/py) of the same at reflux temperature gave IIIb, m.p. 125–28°C (d), C₃₄H₅₆O₄ (M⁺ 528) (Found: C 77.05; H 10.50; C₃₄H₅₆O₄ reqd C 77.27; H, 10.60%); (α)²D +75° (CHCl₃); IR: 1740 (acetate carbonyl); PMR (δ): 2.00 and 2.02 (s, 2 x OAc).

From the above data the genin was assigned as Ia which was identical to aglaiol [14] (m.p., m.m.p. and Co-TLC) isolated from the leaves of Agyrax odorata, lit. m.p. 113–14°C). Periodate oxidation [15] consumed 3 mol of periodate and liberated 2 mol of HCO₂H per mol of (I) indicating the presence of saccharide in pyranose form of the sugars. Methylated saponin (Hakomori's method) [16] followed by acid hydrolysis (N-H₂SO₄) afforded Ia (m.m.p. and Co-TLC) and sugars 2,3-di-O-methyl-D-xylene and 2,3,4-tri-O-methyl-L-rhamnose (RG values and Co-paper chromatography). The sequence of the sugars in the saponin was established by partial acid hydrolysis which resulted in the formation of L-rhamnose first (Co-PC) as an end sugar and prosaponin Ic. This prosaponin on complete acid hydrolysis yielded D-xylene (Co-PC) and Ia (m.m.p. and Co-TLC). Hence the structure of the saponin can be represented as (I).

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NOVEL SYNTHESIS OF BENZOFURANS

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Several substituted 4-chlorocoumarins (II) have been prepared from the corresponding 4-hydroxycoumarins (I) and converted to the respective benzofuran-2-carboxylic acids (III) and then to benzo-furans (IV) by Perkin-Fittig-Ebert method. 1, 2.

1 R = OH III R = COOH
II R = Cl IV R = H

a. R₁ = R₂ = H, R₃ = R₄ = Me.
b. R₁ = R₂ = H, R₃ = R₄ = Me.
c. R₁ = R₂ = H, R₃ = R₄ = Me.
d. R₁ = R₂ = H, R₃ = Me, R₄ = i. Pr.

4-Chlorocoumarins (II) were prepared by reacting the corresponding 4-hydroxycoumarins (I) obtained by the method described earlier, 1 with phosphoryl chloride in 45–60 per cent 10. Respective 4-chloro-3,3',4',4'-tercoumarins accompanied the chlorocoumarins 5.

4-Chloro-6,8-dimethylcoumarin 6 [IIa, m.p. 150–51°C, UV λ max (log ε) 245(3.91), 288(4.19), 325(3.81)] IR KBr (cm⁻¹), 1720(m), 1660(s), 1615(s), 1575(m), 775(m) in dioxane when refluxed for one hour with aqueous sodium hydroxide (10%) gave 5,7-dimethylbenzofuran-2-carboxylic acid [IIa, m.p. 259–60°C, UV λ max (log ε) 230(4.06), 270(4.16), IR KBr (cm⁻¹) 1700(s), 1566(s), 1420(s), 1315(s), 1205(s)].

Similarly, 6,7-dimethyl- [IIb, m.p. 143–44°C, UV λ max (log ε) 235(3.90), 288(4.24), 325(3.81)], 5,8-dimethyl- [IIc, m.p. 82–83°C, UV λ max (log ε) 242(3.89), 303(4.13)] and 5-methyl-8-isopropyl- [IIId, m.p. 83–84°C, UV λ max (log ε) 245(4.01), 297(4.25), IR KBr (cm⁻¹) 1720(s), 1600(m), 1575(s), 780(m)]-4-chlorocoumarins gave respectively 5,6-dimethyl- [IIib, m.p. 243–44°C, UV λ max (log ε) 272(3.97)], 4,7-dimethyl- [IIId, m.p. 205–07°C, UV λ max (log ε) 270(4.25), 285(4.15), IR KBr (cm⁻¹), 1685(s), 1570(s), 1565(s), 1420(s), 1315(s), 1205(s)].