CHEMICAL INVESTIGATION OF THE STEM BARK OF *APHANAMIXIS POLYSTACHYA*

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THE plant *Aphanamixis polystachya* (syn. *Amoora rohituka*) is a medicinal plant employed in our indigenous system of medicine[1,2]. 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[3,4]. 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*[5] and was found to contain aphanamixin.

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°). The pet. ether extract gave a mixture of three compounds (on TLC) which were separated on Al_2O_3 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°, $(\alpha)_D^{25}+4.2°$ ($CHCl_3$), $C_{41}H_{68}O_{10}$. It gave characteristic reactions of a saponin. Acid hydrolysis (7% H_2SO_4) of the saponin afforded a genin, Ia and L-rhamnose and D-xylose (CO-PC).

The genin, m.p. 112–13°, $(\alpha)_D^{25}+53°$ ($CHCl_3$), $C_{30}H_{50}O_2$ (M^+442), gave all the positive tests for a terpene[6-8] and decolourized bromine water in CCl_4; UV; 170 nm, (ϵ212)[9] (disubstituted double bond); IR (principal bands): hydroxyl[10] (3580 and 3453), vinylic (3050 and 1639) probably as $C=CH_2$ (880) cm^{-1}; PMR ($CDCl_3$, 90 MHz, Me_4Si, δ): 0.76 (4α-Me), 0.85 (4β-Me), 0.87 (14α-Me), 0.98 (8β-Me), 0.99 (10β-Me), 1.25 and 1.32 (25-Me_2), 2.75 (symmetrical t, 24-H), 3.25 (m, 3α-H, a carbon atom bearing oxygen) and 4.75 (bs, 21-CH_2). The low field absorptions of 2 × 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[11,12]. The mass spectrum of Ia showed the fragments at m/e 442 (M^+), 427 (M^+-Me), 424 (M^+-H_2O), 409[M^+-(Me + H_2O)], 343 (M^+-$C_6H_{11}O$), 344 (M^+-$C_6H_{12}O$), 317 (M^+-$C_8H_{13}O$), 318 (M^+-$C_8H_{14}O$), 189 and 187.

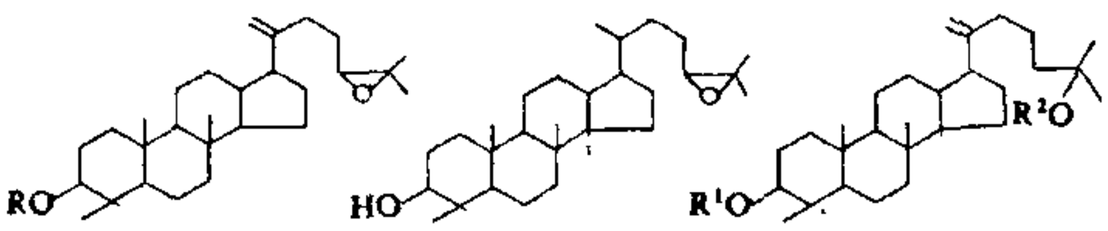
Ia formed an acetate (Ac_2O/py), Ib at room temperature (30 hr), m.p. 160–62°, $C_{32}H_{52}O_3$ (M^+ 484) (Found; C, 79.32; H, 10.75; $C_{32}H_{52}O_3$ reqd., C, 79.34; H, 10.74%), $(\alpha)_D^{30}+68°$ ($CHCl_3$); IR: 1740 cm^{-1}; PMR (δ): 2.01 (acetate methyl), 4.50 (3α-H)[13] and other usual signals.

Reduction of Ia with Pd-C gave II, m.p. 112–15°, $C_{30}H_{52}O_2$ (M^+ 444) (Found C, 81.00; H, 11.70; $C_{30}H_{52}O_2$ reqd., C, 81.08; H, 11.71%), $(\alpha)_D^{30}+6°$ ($CHCl_3$); PMR, (δ), 8 × 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°, $C_{30}H_{52}O_2$ (M^+ 444) (Found; C, 81.02; H, 11.69; $C_{30}H_{52}O_2$ reqd., C, 81.08; H, 11.71%), $(\alpha)_D^{30}+50°$; IR: 3500 (OH), 3055, 1640 and 887 (vinylic) cm^{-1}; PMR (δ), 0.77, 0.84, 0.87, 0.95, 0.98, 1.20 and 1.28, 7 × Me; 4.70, vinylic-H and 3.22, bm, 3α-H.

The acetylation (Ac_2O/py) of III at room temperature afforded III a, m.p. 138–39°, $C_{32}H_{54}O_3$ (M^+486) (Found; C, 79.00; H, 11.00; $C_{32}H_{54}O_3$ reqd., C, 79.01; H, 11.11%), $(\alpha)_D^{30}+70°$ ($CHCl_3$); IR: 3500 (OH) and 1735 (acetate carbonyl); PMR, (δ): 2.00 (s, 1 × OAc) while the acetylation (Ac_2O/py) of the same at reflux temperature gave IIIb, m.p. 125–28° (d), $C_{34}H_{56}O_4$ (M^+ 528) (Found: C 77.05; H 10.50; $C_{34}H_{56}O_4$ reqd C 77.27; H, 10.60%), $(\alpha)_D^{30}+75°$ ($CHCl_3$); IR: 1740 (acetate carbonyl); PMR, (δ): 2.00 and 2.02 (s, 2 × 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 *Aglaia odorata*, lit. m.p. 113–14°). Periodate oxidation[15] consumed 3 mol of periodate and liberated 2 mol of HCO_2H per 1 mol of (I) indicating the presence of disaccharide in pyranose form of the sugars. Methylated saponin (Hakomori's method)[16] followed by acid hydrolysis (N-H_2SO_4) afforded Ia (m.m.p. and Co-TLC) and sugars 2,3-di-O-methyl-D-xylose 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-xylose (Co-PC) and Ia (m.m.p. and Co-TLC). Hence the structure of the saponin can be represented as (I).

The authors express their gratitude to Director, C.D R.I. Lucknow for spectral data and microanalysis,



I ; R = rhamnosyl (1 → 4) xyloside
Ia; R = H
Ib; R = Ac
Ic; R = xylose

II

III; $R^1 = R^2 = H$
IIIa; R^1 = Ac; $R^2 = H$
IIIb; $R^1 = R^2$ = Ac

to Dr (Mrs.) Savitri Devi Srivastava, for her valuable suggestions and Ministry of Health and Family welfare (New Delhi) for award of fellowship to VKA.

21 May 1984; Revised 10 August 1984

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NOVEL SYNTHESIS OF BENZOFURANS

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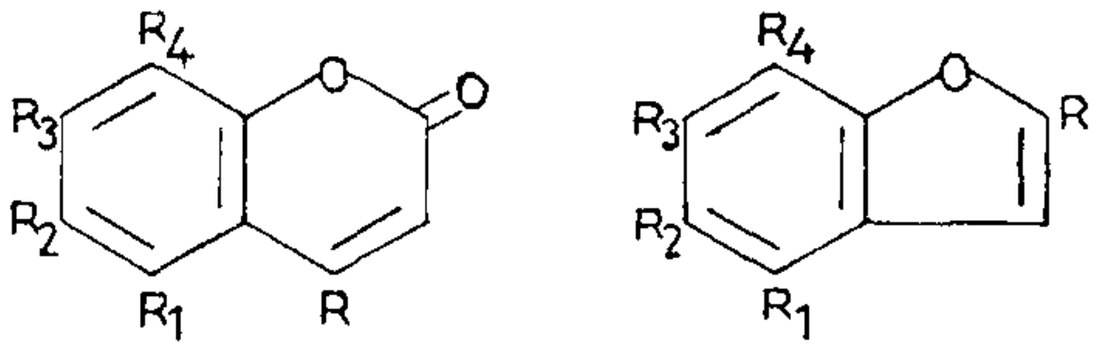
SEVERAL substituted 4-chlorocoumarins (II) have been prepared from the corresponding 4-hydroxycoumarins (I) and converted to the respective benzofuran-2-carboxylic acids (III) and then to benzofurans (IV) by Perkin-Fittig-Ebert method[1,2].



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

a, $R_1 = R_3 = H$, $R_2 = R_4$ = Me.
b, $R_1 = R_4 = H$, $R_2 = R_3$ = Me.
c, $R_2 = R_3 = H$, $R_1 = R_4$ = Me.
d, $R_2 = R_3 = H$, R_1 = Me, R_4 = i.Pr.

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

4-chloro-6,8-dimethylcoumarin[6] [IIa, m.p. 150–51°, UV λ_{max}^{EtOH} (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 [IIIa, m.p. 259–60°, UV λ_{max}^{EtOH} (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°, UV λ_{max}^{EtOH} (log ε), 235(3.90), 288(4.24), 325(3.81)], 5,8-dimethyl- [IIc, m.p. 82–83°, UV λ_{max}^{EtOH} (log ε) 242(3.89), 303(4.13)] and 5-methyl-8-isopropyl- [IId, m.p. 83–84°, UV λ_{max}^{EtOH} (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° UV λ_{max}^{EtOH} (log ε), 272(3.97)], 4,7-dimethyl- [IIIc, m.p. 205–07° UV λ_{max}^{EtOH} (log ε), 270(4.25), 285(4.15), IR KBr (cm^{-1}), 1685(s), 1570(s),