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STIGMASTA-5, 22-DIENE-3β-O-β-D-GLUCOPYRANOSIDE, A NEW SAPONIN FROM THE ROOTS OF *SAPIUM INSIGNE*

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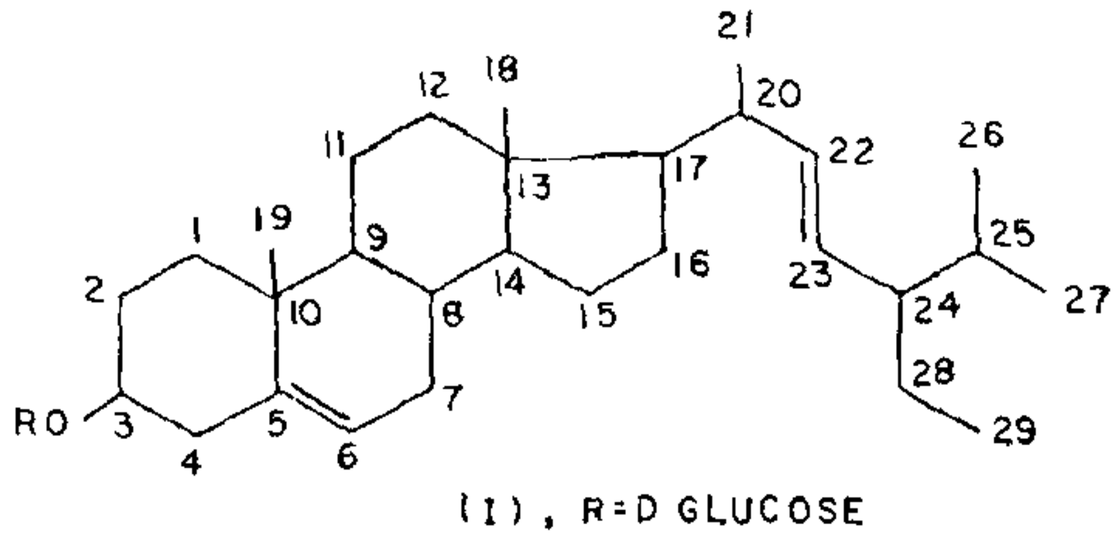
THE plant *Sapium insigne* is full of an acrid milk which when applied to the skin, produces vesication[1,2]. We have examined the roots of *Sapium insigne* and isolated a new saponin; stigmasta-5, 22-diene-3β-O-β-D-glucopyranoside (I) which is the first report in nature.

A reddish brown amorphous compound, m.p. 128–130°C (dec.) molecular formula $C_{35}H_{58}O_6$, $(\alpha)_D^{30} + 16.0°$ ($CHCl_3$), gave characteristic saponin reactions: copious lather with H_2O and haemolysed red blood cells. Acid hydrolysis (7 % H_2SO_4) of the saponin afforded a genin and D-glucose (co-paper chromatography and osazone formation). The genin had m.p. 153–155°, $(\alpha)_D^{25} - 49°$ ($CHCl_3$), $C_{29}H_{48}O$ (M^+ at m/e 412).

From the study of IR, ^1H NMR, mass, acetate derivative oxidation[3], reduction (H_2-Pt), Oppenauer oxidation[4,5] and ozonolysis[6] of the genin confirmed its identity as poriferasterol which was finally confirmed by co-chromatography with an authentic sample[7,8]. Periodate oxidation[9] consumed 2 mol of periodate with the production of 1 mol of HCO_2H per 1 mol of the saponin indicating the presence of monosaccharide in pyranose form of the sugar.

The methylated saponin[10] on acid hydrolysis afforded poriferasterol (m.p., m.m.p. and Co-TLC) and 2,3,4,6-tetra-O-methyl-D-Glucose (Co-PC). The almond emulsin enzyme hydrolysis of the saponin yielded poriferasterol (m.p., m.m.p. and Co-TLC) and D-glucose confirming the β-linkage between the genin and D-glucose.

Hence the structure of the new saponin was assigned as (I)



(I), R=D GLUCOSE

Isolation and Purification: Air-dried and powdered roots (3 kg) of *Sapium insigne*, procured from the United Chemicals and Allied Products, Calcutta (India) were exhaustively extracted three times with ethanol (using fresh alcohol each time) under reflux for 30 days. The total ethanolic extract (30 l) was concentrated to 500 ml under reduced pressure to give a solid mass (yield 3 g) which was extracted with petroleum ether and benzene respectively. The petroleum ether extract did not yield any compound hence it was rejected. The C_6H_6 extract was purified over Al_2O_3 column (C_6H_6: $CHCl_3$, 1 : 1) and crystallized as reddish brown amorphous solid ($CHCl_3$) (yield 1.8 g), m.p. 128–30° (dec.); TLC (Si-gel): Rf 0.67 (C_6H_6: MeOH, (4:6) and 0.82 ($CHCl_3$: MeOH, 7:3), (Found; C, 73.08; H, 10.00; $C_{35}H_{58}O_6$ reqd., C, 73.10; H, 10.54 %). The saponin (1 g) was hydrolysed with 7 % H_2SO_4 (50 ml) as usual which yielded a genin and D-glucose [Co-PC and osazone, m.p. 203–4°, lit. m.p. 204–5°].

Study of the genin: (Found; C, 84.42; H, 11.62; $C_{29}H_{48}O$ reqd; C, 84.46; H, 11.65 %); IR ν_{max}^{KBr} 3400, 3050, 2950, 2870, 1640, 1630, 1425, 1390, 1060, 1050, 1000, 980, 972, 953, 837 and 800 cm^{-1}; ^1H NMR ($CDCl_3$, TMS, 60 MHz) δ 0.68 (d, J = 6.0 Hz, 6H, 2 × CH_3, C-26 and C-27), 0.74 (s, 6H, 2 × CH_3, C-18 and C-19), 0.90 (t, J = 6.0 Hz, 3H, 1 × CH_3, C-29), 0.95 (d, J = 5.0 Hz, 3H, 1 × CH_3, C-21), 1.2–2.00 (complex pattern, polymethylene, CH_2 and CH protons), 2.32 (s, OH), 4.48 (m, 1H, C-3), 5.12 (q, J = 4.0 and 8.0 Hz, 2H, C-22 and C-23), and 5.50 (dd, J = 4.0 and 8.0 Hz, 1H, C-6) respectively. MS: (at m/e); 412 (M^+); 397 (M^+ − Me); 394 ($M^+ - H_2O$); 379 [$M^+ - (CH_3 + H_2O)$], 369 ($M^+ - C_3H_7$); 299 ($M^+ - C_8H_{17}$); 298 ($M^+ - C_8H_{17} - H$), 286 ($M^+ - C_9H_{18}$); 273 ($M^+ - C_{10}H_{19}$ *i.e.* side chain); 259 ($M^+ - C_{11}H_{21}$), 257 [$M^+ - (C_{11}H_{21} + 2H)$]; 246 ($M - C_{11}H_{18}O$) and 231 [$M^+ - (C_{11}H_{18}O + CH_3)$]; mono acetate ($Ac_2O$/py), m.p. 144-146° (lit. m.p. 146-47°), (Found; C, 84.90; H, 11.00; $C_{31}H_{50}O_2$ reqd. C, 84.93, H, 11.01 %); monobenzoate, m.p. 140-41°

(lit. m p. 141°)[7], (Found; C, 83.70; H, 10.00; $C_{36}H_{50}O_2$ reqd. C, 83.73; H, 10.07 %); reduction (100 mg of genin + 100 mg Pt catalyst and 20 ml glacial AcOH, shaken with H_2 for 10 hr), m.p. 142–44°, (lit, m.p. 143°)[7], (Found, C, 83.60; H, 12.48; $C_{29}H_{52}O$ reqd; C, 83.63; H, 12.50 %); oppenauer oxidation [100 mg of genin + 5 ml C_6H_{12} + 120 mg $(Me_2CHO)_3$ Al + 10 ml Ph-Me], m.p. 76–80° (lit. m.p. 80°)[7], (Found; C, 84.88; H, 11.20; $C_{29}H_{46}O$ reqd; C, 84.87; H, 11.21 %); ozonolysis (100 mg of genin + 10 ml gl AcOH + O_3 ca 2 %, as usual) followed by p-NO_2-Ph-NH-NH_2 treatment gave α-ethylisovaleraldehyde, m.p. 85–87° (dec.) [lit. m p. 85–88° (dec.) and Co-TLC][7]. (Found; C, 62.40; H, 8.00; N, 16.82; $C_{13}H_{20}N_3O_2$ reqd; C, 62.40; H, 8.00; N, 16.80 %).

Permethylation and hydrolysis of the saponin

The saponin (100 mg) was methylated by Hakomori's method as usual which afforded a methylated saponin, m.p. 130–32°. The methylated saponin was hydrolysed with acid (7 % H_2SO_4) and worked up as usual which gave poriferasterol (m.p., m.m.p. and Co-TLC) and 2,3,4,6-tetra-O-methyl-D-glucose (RG 1.00 in *n*-BuOH: EtOH: H_2O, 5:1:4, lit. RG 1.00 *in n-BuOH: EtOH: H_2O, 5:1:4).*

Periodate oxidation of the saponin

A solution of saponin (30 mg) in ethanol (15 ml) was treated with 0.1 M $NaIO_4$ solution. The periodate consumed and formic acid liberated were estimated by standard procedure which corresponded to 2 and 1 mol respectively.

Enzymatic hydrolysis:

The saponin (100 mg) in ethanol (20 ml) was treated with almond enzyme solution. The liberation of D-glucose was detected by paper chromatography (Co-PC).

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CLASTIC DYKE AND THE ASSOCIATED ZEOLITE VEINS IN TALCHIR DEPOSITS, SARGUJA DISTRICT, MADHYA PRADESH

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WHILE working on Talchir deposits of Madhaya Pradesh, the authors came across a clastic dyke in Gungatta river, about 15 km south of Ambikapur town. It is exposed on the left bank of the river, 1.5 km downstream from Shayam Gungatta dam site. It cuts across the sandstone and shale beds of basal Talchir Group (figure 1). The trend of the dyke is 312° with a dip about 90°. The maximum width is about 1.5 m and it extends over a distance of 15 m and both the ends are covered by soil.

The sandstone and shale beds on either side of the dyke are undisturbed and do not show any sign of deformation. The dip and strike directions of the beds are 15° NW and 225°, respectively. The dyke consists of sandy material but the grain size is finer than the associated sandstone beds.

The clastic dykes have been reported earlier from India[1,2] and other parts of the world[3–6] but the remarkable feature of this clastic dyke is the occurrence of zeolite veins penetrating throughout the body of the dyke. The major zeolite veins run parallel to the strike of the dyke but small and thin veins cut the dyke at 90°. On both sides, the dyke is bounded by thick zeolite veins. The thickness of the veins generally decreases downward. In the upper part of the dyke, the thickness is about 15 cm; however, in the lower part it