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Chemical Constituents of *Dalbergia paniculata* Roots

M. RADHAKRISHNIAH

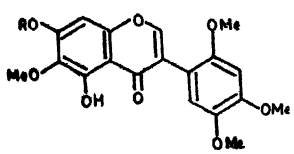
Department of Chemistry, Besant Theosophical College, Madanapalle (A.P.) India,

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Caviunin, caviunin-7-O-glucoside, triacontane and cyclitol monomethyl ether, (+)-pinitol, were isolated from the roots of *Dalbergia paniculata*. The structure of the new glycoside, Caviunin-7-O-glucoside was established by spectral data and synthesis.

EARLIER investigation[1,2] on the seeds of *Dalbergia paniculata* has revealed the presence of two new rotenoids in the genus *Dalbergia*. A chemical examination of the roots of *Dalbergia paniculata* was undertaken to find out the possible precursors for the formation of these piscicidal constituents.

The dried root shavings of *Dalbergia paniculata* were extracted successively with light petroleum ether, benzene and acetone, From the benzene extract, a known isoflavone, Caviunin[3] (I) was obtained by alkali fractionation. The neutral fraction of the benzene extract afforded a crystalline solid, which was identified as Triacontane[4], by spectral and analytical data.



I R=H

II R=Glucosyl

The acetone extract has yielded two crystalline compounds. One of these compounds analysed for $C_7H_{14}O_6$ and was identified as (+)-pinitol[5,6] from its physical constants and spectral properties (*vide* experimental).

The second crystalline compound, $C_{25}H_{28}O_{15}$, m. p. 236-7° gave a pink colour with sodium amalgam and hydrochloric acid (Wolfrom test)[7] and a positive Molisch test, but Shinoda[8] and Durham[9] tests were negative. These colour reactions and the u. v. data, λ_{max} 263 and 294 nm (log ϵ 4.30 and 3.09), clearly indicated the isoflavone nature of the compound. The glycosidic nature of the compound[10] was reflected by strong absorption bands at 1060 and 1120 cm^{-1}. Acid hydrolysis of the compound afforded glucose and an aglycone, identified as caviunin. Green colouration with ferric chloride, as well as, carbonyl absorption at 1660 cm^{-1} shown by the glycoside revealed the presence of chelated hydroxyl at 5C-position. This was supported by the bathochromic shift (12 nm) of the absorption maximum at 263 nm in the presence of aluminium chloride[11] and appearance of one hydroxyl proton at δ 12.57 (exchangeable in D_2O) in the n. m. r. spectrum. Hence the isoflavone glycoside should have the glucose residue only at the 7-position. This conclusion was supported by the fact that in the u. v. spectrum of the glycoside there occurs no bathochromic shift of the absorption maximum by the addition of sodium acetate[12].

The mass spectrum of the compound was similar to that obtained with caviunin (M^+374, 100%) owing to the easy elemination of the sugar moiity observed with the *o*-glycosyl compounds[13]. The n. m. r. spectrum of the compound taken in DMSO-d_6 showed all the signals as singlets (*vide* experimental). On the basis of the above spectral evidence[14] the compound was given the structure II.

To confirm the structure assigned to the new isoflavone glycoside, synthesis of 7-glucosyloxy-5-hydroxy-2',4',5', 6-tetramethoxyisoflavone was carried out starting from caviunin, by treating with acetobromoglucose and potassium hydroxide in acetone medium[15].

Experimental

Melting points are uncorrected. Infrared spectra were measured in KBr pellet and the ultraviolet spectra in methanol solution. N.m.r. spectra were recorded in Varian Spectrometer operating at 60 and 100 MHz.

Isolation of the constituents of Dalbergia paniculata *Roots*:

The dried shavings of *Dalbergia paniculata* (100 g) were successively soxhleted with light petroleum (60-80°), benzene and acetone.

The light petroleum extract on concentration deposited a cream coloured solid. It was dissolved in boiling benzene and precipitated by light petroleum to yield a colourless waxy, crystalline,

aliphatic long-chain alcohol (1). From the residual extract no other crystalline matter was obtained.

The benzene extract was concentrated to 100 ml and set aside for few days. It did not deposit any solid. The concentrate was taken in ethyl acetate (200 ml) and extracted successively with 2% and 10% aqueous sodium carbonate and then with 4% aqueous sodium hydroxide. The 2% sodium carbonate extract on acidification with hydrochloric acid gave a pink coloured solid. This solid was purified over a column of neutral alumina (20 g), employing methanol as eluant when isoflavone, caviunin (2) was obtained. The other two alkali fractions when acidified did not yield any solid. Finally, most of the organic solvent was removed from the neutral fraction when triacontane (3) was obtained as a white glistening crystalline solid.

The acetone extract was concentrated (100 ml) and set aside. An oily layer collecting at the bottom solidified when kept in the refrigerator for 5 days. This solid on crystallisation from absolute ethanol containing few drops of acetic acid yielded (+)-pinitol (4) as octahedral prisms. The acetone mother liquor after the separation of (+)-pinitol was evaporated to dryness and macerated with dry ether. The dark red solid thus obtained was dissolved in dry methanol (15 ml) and set aside. Caviunin-7-*o*-glucoside (5) was obtained as a colourless solid. The mother liquor after the separation of this compound on further concentration did not yield any other crystalline solid.

(1) Aliphatic long-chain alcohol : (300 mg, 0.003%), colourless waxy crystals, m.p. 94-5°, ν_{max} 3425 cm^{-1}.

(2) Caviunin : (60 mg, 0.0006%), colourless needless, m. p. 190-91°. m/e 374, λ_{max} 223 (4.52), 263 (4.47), 297 (4.26), 360 infl. (3.53) nm (log ϵ) : λ_{max} ($AlCl_3$) 224, 275, 298, 380 infl. 400 sh. : ν_{max} 3435, 1675, 1637 cm^{-1}. N.m.r. (60 MHz) in $CDCl_3$ δ 3.78 (s, 2'C-OCH_3), 3.84 (s, 4'C-OCH_3), 3.92 (s, 5'C-OCH_3), 4.01 (s, 6C-OCH_3), 6.48 (s, 8C-H), 6.62 (s, 3'C-H), 6.87 (s, 6'C-H), 7.85 (s, 2C-H).

(3) Triacontane : (100 mg, 0.001%), white glistening crystalline solid, m. p. 66°, m/e 422. ν_{max} 2950, 2923, 2900, 2857, 1475, 1468, 1380, 875 cm^{-1}.

(4) (+)-Pinitol : (800 mg, 0.008%) octahedral prisms, m. p. 187°. $[\alpha]_D^{31}$ +67 (c, 1.0 in water). ν_{max} 3420, 3330 br. cm^{-1}. N. m. r. (100 MHz, AcOH) 3.2-4.5) Complex multiplet), 3.63 (s, -OCH_3).

(5) Caviunin-7-o-glucoside : (40 mg, 0.0004%). It crystallised from ethanol as colourless fibre-like crystals, m. p. 236-7°. λ_{max} 263 (4.30) and 294 infl. (3.09)nm (log ϵ) ; λ_{max} 242 (4.08) and 282 (3.98) nm (log ϵ) : λ_{max} (NaOAc) 263 and 294 infl. nm λ_{max} ($AlCl_3$) 275 and 300 infl. nm: λ_{max} (H_3BO_3-NaOAc) 263 and 294 infl. nm ν_{max} 3440, 3340 br., 1660, 1623, 1120 br, 1060, 1030, 995 cm^{-1}. N. m. r. (100 MHz, DMSO-d_6) σ 3. 72 (s, 2'C-OCH_3), 3.75 (s, 4'C-OCH_3), 3.86 (6H, s, 5'C-OCH_3 and 6C-OCH_3), 3.3_5.5 (sugar protons), 6.73 (s, 8C-H), 6.81 (s, 3'C-H), 6.94 (s, 6'C-H), 8.35 (s, 2C-H, 12.57 (s, 5C-OH).

On chromatograms it appeared as a dark purple spot when viewed under u. v. light. When sprayed with alcoholic ferric chloride it developed a green colour, and with diazotised sulphanilic acid an orange colour. Paper chromatography [descending (*n*-butanol-acetic acid-water, 4 : 1 : 5 v/v, upper)] R_F0.72, t. l. c. [Kieselgel G, (benzene-dioxane-acetic acid, 90 : 25 : 4 v/v)], R_F 0-65, t. l. c. [Polyamide (ethanol-water, 3 : 2 v/v)] R_F 0.89.

Acetylation of Caviunin-7-o-glucoside : (Penta-acetate)

A mixture of the compound (6mg), acetic anhydride (0.3 ml) and freshly fused sodium acetate (40 mg) was heated on a steam bath for 2 hrs. The contents were cooled, poured over crushed ice (10 g) and the resulting solid filtered and dried. It crystallised as colourless needles from ethanol m. p. 102-4° (Found C, 54.43, H, 5.25. $C_{35}H_{38}O_{18}.H_2O$ requires C, 54.96, H, 5.24%). λ_{max} 261 and 293 infl. nm. ν_{max} 1745 and 1645 cm^{-1}.

Acid hydrolysis of the glucoside : (Caviunin and glucose).

A solution of caviunin-7-*o*-glucoside (8 mg) in 7% aqueous sulphuric acid (5 ml) and methanol (0.5 ml) was heated on a water bath for 3 hrs. Methanol was then distilled off and the residue cooled. The aqueous solution was extracted with chloroform (3 × 5 ml). The chloroform extract was washed with water, dried over anhydrous sodium sulphate and the solvent removed. The resulting solid was crystallised from aqueous ethanol to yield colourless needles (5 mg), m. p. 190-91° either alone or when admixed with an authentic sample of caviunin. Identity of the compound as caviunin was substantiated by chromatographic and spectral comparison.

The aqueous part was evaporated to dryness. The syrupy product when examined by paper chromatography [descending, butanol-acetic acid-water (4 : 1 : 5 v/v, upper), aniline phthalate spray] showed a pink spot with R_F 0.20. The sugar was identified as glucose by comparison with an authentic sample.

Synthesis of 7-glucosyloxy-5-hydroxy-2', 4', 5', 6-tetra-hydroxyisoflavone :

To a solution of caviunin (100 mg) in acetone (10 ml) 0.5 ml of 9% aqeous potassium hydroxide was added and to this mixture acetobromoglucose (140 mg in 5 ml) acetone was slowly added with stirring and cooling in an ice bath. The mixture

was then shaken for 14 hrs. and poured into water (100 ml) with stirring. The aqueous solution after neutralisation with hydrochloric acid was repeatedly extracted with chloroform to remove the unchanged caviunin. The resulting solution was flash evaporated and the residue crystallised from ethanol to yield colourless crystals melting at 236-7°, alone or when admixed with the natural sample of caviunin-7-*o*-glucoside. The identity of the synthetic sample with the natural sample was further established by chromatographic and spectral data.

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