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ISOCAVIUNIN 7-GENTIOBIOSIDE, A NEW ISOFLAVONE GLYCOSIDE FROM *DALBERGIA SISSOO*

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Many new compounds have previously been reported from different parts of *Dalbergia sissoo* [1–4]. We now report the isolation of a new isoflavone diglucoside, isocaviunin 7-*O*-gentiobioside. The new glycoside analysed for $C_{31}H_{38}O_{18}$, did not respond to Shinoda's test but gave a red colour in Na–Hg/HCl test, violet colour with $FeCl_3$ and a positive Molisch's test. These colour reactions suggested it to be an isoflavone glycoside with a free hydroxyl at the 5-position. On Si gel TLC with solvent systems $CHCl_3$–MeOH (7:3); and EtOAc–MeOH (1:1) it showed on exposure to iodine vapours a single yellow colour spot which on keeping changed to green. Hydrolysis with 7% aq. H_2SO_4, yielded glucose and an aglycone which gave a shift of +10 nm with NaOAc in UV (absent in the glycoside) thus showing that the sugar is linked to 7-position of the aglycone. That it is a diglucoside was indicated by the NMR of the glycoside acetate which showed multiplets at δ 2.1 integrating for 21 protons due to seven acetoxyl groups and at δ 4.23–5.42 integrating for 14 sugar protons. Other signals in the NMR were singlets at δ 3.73, 3.79, 3.85, 3.90 each integrating for three protons and at δ 6.56, 6.80, 7.14 and 7.78 each integrating for one proton. The aglycone, therefore, contains 4 methoxyls and 4 armoatic protons. A singlet at δ 2.45 for three protons indicated the presence of only one free phenolic hydroxyl in the glycoside. A +15 nm shift in the UV spectra on addition of $AlCl_3$ indicated it to be 5-hydroxyisoflavone. A negative Gibb's test fixed the position of one methoxyl in the A-ring at C-8. Since no *ortho*- or *meta*-coupling is observed, the remaining three methoxyls must be in the B-ring at the 2′, 4′, 5′-positions. The aglycone was identified as isocaviunin on the basis of co-TLC, co-IR and mmp with an authentic sample.

Both glucose units were shown to be in the pyranose form linked by 1 → 6 linkage on the basis of permethylation by Hakomori's method [5] followed by Killiani's hydrolysis when 2,3,4,6-tetra-*O*-methylglucose and 2,3,4-tri-*O*-methylglucose were identified on PC. Hydrolysis of the glycoside with emulsin to give isocaviunin and glucose suggested it to be an *O*-glycoside with β-linkages.

The structure of the new glycoside is thus 5-hydroxy-8,2′,4′,5′-tetramethoxyisoflavone 7-O-β-(1 → 6)-diglucoside, i.e. isocaviunin 7-gentiobioside. This is the first report of an 8-methoxy isoflavone gentiobioside in plants.

EXPERIMENTAL

Defatted pods (600 g) were first extracted with alcohol and then with 50% aq. alcohol. The EtOAc insoluble part of the latter was column chromatographed (Si gel). The EtOAc–MeOH (1:1) eluate was again column chromatographed when $CHCl_3$–MeOH (4:1), as eluting solvent, yielded a yellow compound (200 mg) (R_f 0.8 in $CHCl_3$–MeOH (7:3), 0.37 in MeOH–EtOAc (1:1), mp 170–72°; $[\alpha]_D^{25°}$ (in DMSO): −65.6°; UV λ_{max}^{MeOH} nm: 260; +NaOAc: 260; +$AlCl_3$: 275; +$AlCl_3$+HCl: 275. The acetate crystallized from EtOAc; mp 140–42°; ^1H NMR (90 MHz, $CDCl_3$): δ 2.1 (21H, *m*, -OCOMe), 2.45 (3H, *s*, -OCOMe), 3.73 (3H, *s*, -OMe), 3.79 (3H, *s*, OMe), 3.85 (3H, *s*, -OMe), 3.90 (3H, *s*, -OME), 4.23–5.42 (14H, *m*, sugar protons), 6.56 (1H, *s*, H-6), 6.80 (1H, *s*, H-3′), 7.14 (1H, *s*, H-6′), 7.78 (1H, *s*, H-2).

Hydrolysis of glycoside. Glycoside (25 mg) in MeOH and 7% H_2SO_4 soution was refluxed for 4 hr. Extraction with $CHCl_3$ gave isocaviunin (R_f 0.56 in EtOAc–C_6H_6 (1:4)), mp 193–94°; UV λ_{max}^{MeOH} nm 260; +$AlCl_3$: 275; +NaOAc: 270; and the aq. portion was shown to have glucose by PC.

Permethylation and hydrolysis of glycoside. Glycoside (5 mg) was permethylated with MeI/NaH [5] and the methyl ether (R_f 0.5 in $CHCl_3$) was hydrolysed with Killiani's mixture [6]. On PC, in solvent BEW (5:1:4), two spots were obtained and identified as 2,3,4,6-tetra-*O*-methylglucose and 2,3,4-tri-*O*-methylglucose on comparison with those obtained by repeating the process with glucose and rutin.

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