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CAVIUNIN 7-*O*-GENTIOBIOSIDE FROM *DALBERGIA SISSOO* PODS

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We wish to report the isolation of a new isoflavone glucoside from the mature pods of *Dalbergia sissoo* which has been identified as caviunin 7-*O*-gentiobioside, i.e. the 7-gentiobioside of 5,7-dihydroxy-6,2′,4′,5′-tetramethoxyisoflavone.

EXPERIMENTAL

The air-dried defatted mature pods (600 g) were extracted with alcohol and then with 50% aq. alcohol. The EtOAc insoluble portion of the latter was column chromatographed (Si gel). The EtOAc–MeOH (4:1) eluate contained, in addition to the polymeric impurities, a compound which gave dim red fluorescence. It was obtained in pure form by precipitation with Et_2O (150 mg), mp 210–12°; R_f 0.39 in EtOAc–MeOH (1:1). It analysed for $C_{31}H_{38}O_{18}$, gave violet ferric colour, positive Molisch's test and red colour with Na–Hg followed by HCl, suggesting it to be an isoflavone glycoside. $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3500 (hydroxyl), 1650 (carbonyl). $\lambda_{\max}^{\mathrm{MeOH}}$ nm: 260, 295 sh; $+\mathrm{AlCl}_3$: 275; $+\mathrm{AlCl}_3$ + HCl: 275; +NaOAc: 260, 295 sh; +NaOAc + H_3BO_3: 260, 295 sh; showed the presence of free 5-OH and that the 7-position was occupied. The compound readily underwent hydrolysis with Killiani's mixture [1] when glucose was identified in the aq. hydrolysate by PC, thus suggesting it to be an *O*-glucoside.

On acetylation by the Ac_2O–Py method, the compound gave an acetate, mp 77–78°, the ^1H NMR of which (90 MHz, $CDCl_3$, TMS as internal standard) showed 4 methoxyls at δ 3.7, 3.75, 3.8 and 3.87, multiplets at δ 4.2–5.4 integrating for 14 glucosyl protons and 4 singlets corresponding to one proton each at δ 6.56, 6.81, 7.14 and 7.89. It also showed one phenolic acetoxyl at δ 2.48 and 7 aliphatic acetoxyls at δ 2.0 indicating the compound to be a diglucoside and that two glucose units were linked as a biose to one of the phenolic hydroxyls in the aglycone. On hydrolysis with 7% aq. H_2SO_4, the glycoside gave an aglycone which showed a bathochromic shift of 10 nm with NaOAc, indicating that the biose unit is linked at C-7 position in the aglycone. The compound gave positive Gibb's test thus showing that the C-8 position in the glycoside is free. Absence of any *ortho*- or *meta*-coupling in the ^1H NMR, as shown by 4 one-proton singlets in the aromatic region, indicated that, in addition to C-8, C-2, C-3′ and C-6′ positions are also free and therefore the 4 methoxyls are located at C-6, C-2′, C-4′ and C-5′ positions thereby showing the aglycone to be caviunin. Mass spectra of the glycoside (*m/e* (% abundance); 374 (100%), 359 (60), 343 (16), 331 (26)) however, did not show a molecular ion but an intense peak at *m/e* 374 corresponding to caviunin. The positions of two methoxyls at C-6 and C-2′ were also supported by intense (aglycone − 15) and (aglycone − 31) ions in the mass spectra. The identity of the aglycone was further confirmed by its mp, IR and mp of its acetate and methyl ether [2]. Mild hydrolysis with 0.5% H_2SO_4 for 5 min gave caviunin 7-*O*-β-D-glucopyranoside [3] (identified by comparison with an authentic sample) and glucose.

The inter-sugar linkage in the bioside was established by means of permethylation studies. Permethylation of parent glucoside by Hakomori's method [4] followed by hydrolysis of the permethylate by Killiani's reagent [1] yielded two methylated sugars identified as 2,3,4,6-tetra-*O*-methyl-D-glucose and 2,3,4-tri-*O*-methyl-D-glucose. Thus both glucose units are present in the pyranose form with 1 → 6 inter-sugar linkage and attached to the 7-position of the aglycone by an anomeric OH. The β-configuration of glucosidic linkages was established by means of enzymatic hydrolysis with β-glucosidase. Hence, the compound is caviunin 7-*O*-(β-D-glucopyranosyl-1 → 6-β-D-glucopyranoside).

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