(C=O); δ ($CDCl_3$) 4.9 (methine-H), 1.28 (CH_2 of alcoholic residue), 0.8799 (CH_3) and 2.29 (backbone CH_2).

The viscosity of the polymers was measured using an Ubbelohde viscometer. Solubility of the polymers were tested in different solvents.

Ir spectra (CCl_4) were recorded on a Perkin-Elmer 782 spectrophotometer and ^1H nmr spectra ($CDCl_3$) on a Bruker CXP spectrometer (90 MHz).

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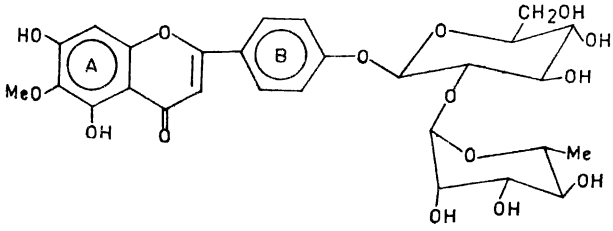
A New Flavone Glycoside from the Roots of *Cassia marginata*

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In continuation of our studies on the phytochemical investigation of *Cassia* species, we now report here the isolation and structure elucidation of a new flavone glycoside from the roots of *Cassia marginata*, a medicinally important plant[1]. The flavone glycoside was characterised as 5,7-dihydroxy-6-methoxy-flavone-4′-O-neohesperidoside (compound 1) on the basis of spectroscopic and chemical studies.



1

Results and Discussion

Compound **1**, m.p. 198—200°, was analysed for $C_{28}H_{32}O_{15}$ (elemental analysis and M^+). The conclusive colour reactions and uv spectrum with different chemical shifts indicated it to be a flavone glycoside. The glycoside on acid hydrolysis yielded a pale yellow aglycone and two sugars indentified as glucose and rhamnose by R_f values 0.18 and 0.34 respectively (pc ; solvent—BAW, 4 : 1 : 5, v/v, spray-AHP) and co-chromatography with authentic sample.

The aglycone, $C_{16}H_{12}O_6$ (M^+ at m/z 300), m.p. 265—67°, responded positive colour tests for flavone. The shifts induced in the uv spectra (MeOH) by $AlCl_3$, $AlCl_3$+HCl, NaOAc, NaOMe and an A_2B_2 system characteristic of a 1,4-disubstituted aromatic ring (B ring) in the pmr spectra of the acetate of aglycone lead us to conclude that the favone bears three free hydroxyls at C-5, C-7, and C-4′. A singlet at δ 3.85 (3H) showed the presence of one methoxyl which was confirmed by the MS with M^+ 300 of the aglycone. The pmr spectra also showed a signal at δ 7.15 due to the single aromatic proton on A-ring, which is evidence for OMe group located at C-6 as the A-ring proton C-8 absorbs around δ 7.20—7.40 in 5,7-diacetoxyflavones and C-6 around δ 6.73—6.85 in 5,7-diacetoxy-8-methoxyflavones irrespective of B- and C-rings substituents[2]. The mass spectrum of the aglycone displayed M^+ at m/z 300 and a peak at m/z 285 corresponding to the loss of methyl from M^+ ion peak. This also justifies the placement of the methoxy at C-6[3]. Finally, the m.p. of the triacetate, m.p. 168—69°[4] and the methylated aglycone (scutellarein methyl ether), m.p. 162—

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63°[5], lead us to concluded that the aglycone is 5,7,4′-trihydroxy-6-methoxyflavone.

The point of attachment of sugar moiety at position-4′ of the flavone (aglycone) was established by colour reaction and spectral studies. Campari-son of uv data of the aglycone (λ_{max} 275, 342 nm) with that of the glycoside (278, 334 nm) revealed a hypsochromic shift of 8 nm in band-I and a bathochromic shift of 3 nm in band-II, indicating the glycosidation at position-4′ of the aglycone[6]. The aromatic acetate methyl signal at δ 2.30 in the aglycone acetate showed the presence of OAc at C-4′ which was absent in the glycoside acetate confirming the glycosidation at the same position. This also indicates that the two sugars, glucose and rhamnose are present in the form of bioside which was confirmed by periodate oxidation of the glycoside. The partial hydrolysis of the glycoside with 7% formic acid in cyclohexanol showed that rhamnose is the terminal sugar in the bioside.

The glycoside was permethylated, hydrolysed and the resulting partially methylated sugars were identi-fied as 2,3,4-tri-*O*-methyl-L rhamnose and 3,4,6-tri-*O*-methyl-D-glucose by the reported method using 2,3,4,6-tetra-*O*-methylglucose as standard[7] and co-chromatography with authentic samples. This established that the inter-sugar linkage is rhamnosyl(1→2)glucose. In the pmr spectrum of the glycoside, a signal at δ 1.15 was observed which is typical of rhamnose methyl group. This confi-rmed the inter-sugar likage in the bioside to be in the form of neohesperidoside[8]. Thus, the structure of compound **1** was established as 5,7-dihydroxy-6-methoxyflavone-4′-*O*-neohesperidoside.

Experimental

All m.ps. are uncorrected. Uv spectra (MeOH) were recorded on a Beckman DU-6 spectropho-tometer, ir spectra (KBr) on a Perkin-Elmer 577 spectrophotometer, pmr spectra ($CDCl_3$) on a Perkin-Elmer R-32 spectrometer (90 MHz) using TMS as internal standard and mass spectra on a Jeol JMS-D 300 spectrometer at 70 eV and 300°.

Air-dried and defatted powedred roots (4 kg) were extracted with hot ethanol. The ethanol extract after concentration under reduced pressure was resolved into ether-soluble and -insoluble parts. The ether-insoluble part was passed through a column of silica gel and eluted with increasing proportion of chloroform and methanol. Elusion of the column with chloroform-methanol (8 : 2, v/v) afforded compound **1** (400 mg). Compound **1** was crystallised from methanol as a colourless plates, m.p. 198—200° (Found : C, 56.15 : H, 5.50. $C_{28}H_{32}O_{18}$ requires : C, 55.26 ; H, 5.26%) ; R_f = 0.42 (pc, BuOH-AcOH-H_2O=4 : 1 : 5, v/v). It gave a green colour with alcoholic ferric chloride, a bright yellow colour with concentrated H_2SO_4 and positive Molisch's test ; λ_{max} (MeOH) 228, 278, 334 nm; (+$AlCl_3$) 242, 308, 376 ; (+$AlCl_3$+HCl) 241, 307, 376 ; (+NaOAc) 232, 295, 336 ; (+NaOAc+H_3BO_3) 232, 278, 338 : (+NaOMe) 238, 283, 389 nm ; ν_{max} 3 440 (OH), 2 950 (OMe), 1 655 (chelated C=O), 1 575 and 1 525 cm^{-1} (aromatic) ; *m/z* 608 (M^+) ; of the acetate δ ($CDCl_3$) 1.15 (d, *J* 6 Hz, rhamnose methyl), 1.9—2.13 (18H, s, OAc-rhamno-glucoside), 2.38 (3H, s, OAc at C-5), 2.40 (3H, s, OAc at C-7), 3.90 (3H, s, OMe), 4 00—5.50 (br-sugar protons), 6.37 (1H, s, C-3). 7.15 (1H, d, *J* 2.5 Hz, C-8), 7.22 (2H, d, *J* 9 Hz, C-3′,5′) and 7.88 (2H, d, *J* 9 Hz, C-2′,6′).

The glycoside (200 mg) was hydrolysed with 7% ethanolic H_2SO_4 for 8 h. The aglycone was reco-vered as usual and crystallised from methanol as pale yellow needles (95 mg), m.p. 265—67° (Found: C, 64.75 ; H,4.28. $C_{16}H_{12}O_6$ requires : C, 64.00 ; H, 4.00%) ; R_f = 0.86 (pc, BAW, 4 : 15, v/v) and 0.71 (pc, 30% AcOH) ; ν_{max} (MeOH) 226, 275, 342 nm ; (+$AlCl_3$) 240, 306, 386 ; (+$AlCl_3$ +HCl) 240, 306, 386 ; (+NaOAc) 230, 294, 343 ; (+NaOAc + H_3BO_3) 230, 274, 347 ; (+NaOMe) 240, 280, 397 nm ; ν_{max} 3 450 (OH), 2 960 (OMe), 1 650 (chela-ted C=O), 1 570 and 1 520 cm^{-1} (aromatic) ; *m/z* 300 (M^+, 32%), 285 (M^+-Me, 28%), 282 (26), 257 (49), 167 (28), 159 (29), 139 (100), 119 (55), 89 (23) and 70 (90). Acetylation of the aglycone gave a triacetate, m.p. 168—69°, δ ($CDCl_3$) 7.86 and 7.23 (A_2B_2 system, 4H, d, *J* 9 Hz, C-2′,6′ and C-3′, 5′), 7.15 (1H, d, *J* 2.5 Hz, C-8), 6.35 (1H, s, C-3), 3.85 (3H, s, OMe), 2.45 (3H, s, OAc at C-7), 2.35 (3H, s, OAc at C-5) and 2.30 (3H, s, OAc at C-4′).

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