Asian Journal of Chemistry Vol. 5, No. 4 (1993), 1148–1150
NOTES

A Flavone Glycoside, Robinitin-7-O-β-D-Glucopyranoside from *Alternanthera sessilis*

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The present paper deals with the isolation and structural elucidation of a flavone glycoside robinitin-7-*O*-β-D-glucopyranoside.

Alternanthera sessilis is a sea-spreading herb. It is chiefly distributed in the warmer parts of India[1]. The plant is reported to be used as diuretic[2]. The present paper deals with the isolation and structural elucidation of a flavone glycoside, robinitin-7-*O*-β-D-glucopyranoside(II) on the basis of chemical and spectral evidences.

The air dried and powdered leaves of *Alternanthera sessilis* were extracted exhaustively with rectified spirit and the extract was concentrated to a dark brown viscous residue. The dark brown viscous mass was then treated successively with pet. ether, benzene, chloroform, ethylacetate and acetone in the order of their increasing polarity. The chloroform and ethylacetate fractions were found to be identical on TLC over silica gel and they were therefore mixed. The combined extract was concentrated to a yellow amorphous mass which on TLC examination in toluene–ethylacetate–formic acid (5 : 4 : 1) showed a single spot which on crystallization from MeOH gave compound I as yellow needles. Compound I responded to all positive tests of flavone glycoside.[3] Elemental analysis agreed to the molecular formula $C_{21}H_{20}O_{12}$ m/z $[M]^+$ 302, m.pt. 225–27°C. Its IR spectrum displayed strong bands (cm^{-1}) at 3356 (OH), 2980 (C–H), 1690 (C=O), 1135 (C–O). The ultraviolet spectrum showed absorption maxima at 250, 265, 320 sh, 360 nm and changes in the presence of customary shifts reagent[4,5] suggested free hydroxyl groups at 3′,4′,5′-positions with blocked C–7 position as it does not give bathochromic shift with NaOAc.

On acid hydrolysis with 7% HCl, I gave an aglycone (1a), m.pt. 299°C, which was identified as robinitin[6] by comparison of its spectral data and R_f value with known authentic samples. The sugar obtained was identified as D-glucose (PC in four solvents).

Acetylation of I with Ac_2O/py gave a heptaacetate derivative, m.pt. 132°C. The ^1H NMR spectrum of I showed a singlet at 7.42 for two protons and was

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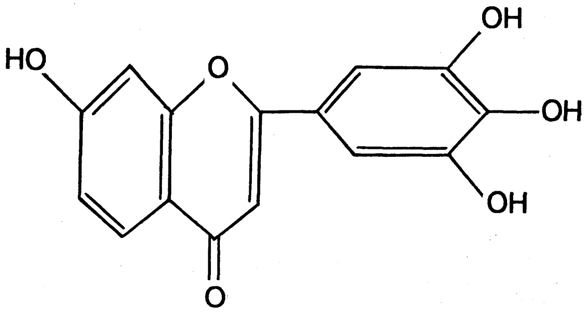
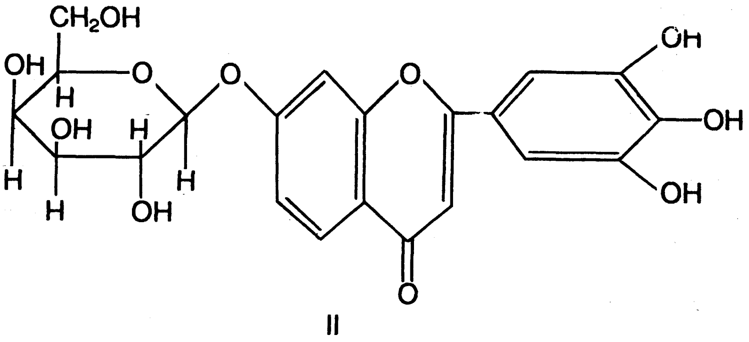
assigned to C–2′,6′ protons. A multiplet consisting of two *meta*-coupled and two *ortho*-coupled doublets was obtained at δ 86.98 and δ 7.40 (J = 8.5 Hz, J = 2.0 Hz) and was assigned to C–5, 6 and 8 protons respectively. The ^{1}H NMR spectrum of I also exhibited a broad singlet at δ 1.78–2.18 for twelve protons, which was assigned to sugar acetoxyls and another singlet at δ 2.32 for nine protons assigned to OAc at 3′, 4′ and 5′ positions.

Methylation of glycoside with MeI/Ag$_2$O/DMF followed by acid hydrolysis with 7% HCl gave a partially methylated aglycone, m.pt. 185°C, which was identified as 7-OH,3′,4′,5′-tri-O-methyl flavone[7](I) by its spectral data and methylated sugar was identified as 2,3,4,6-tetra-O-methyl-D-glucose by co-chromatography with known sample over silica gel (Toluene : MeOH, 4 : 1).

Periodate oxidation of glycoside with NaIO$_4$ showed that sugar is present in pyranose form. Somogyis copper micro-method[8] indicated one mole of sugar/mole of aglycone.



I



II

Compound I, m.pt. 225–27°C crystallized as yellow granules, UV max nm: (MeOH) 250, 265, 320 sh, (+NaOAc) 252, 266, 380 sh, (+NaOAc–H$_3$BO$_3$) 250, 265, 325, (+AlCl$_3$) 250, 267, 388, (+AlCl$_3$–HCl) +2559, 266 sh, 290, 370,

(+NaOMe) 250 sh, 290, 402, ^{1}H NMR (90 MHz, $CDCl_3$); 7.42 (2H, S, H-2′,6′), 6.98 (1 H, d, J = 200 Hz, H-8), 7.12 (1 H, m, J = 2.0 Hz, J = 8.5 Hz, H-6), 7.40 (1 H, d, J = 8.5 Hz, H-5), 2.32 (9 H, S, OAc × 3, aromatic acetoxyls), 1.78–2.18 (12 H, S, OAc × 4, aliphatic acetoxyls). MS data: m/z/M^+ 302.

Acid Hydrolysis of Glycoside

Glycoside I (20 mg) was refluxed with 7% HCl for 2 hrs. at about 100°C. The reaction mixture was then extracted with EtOAc. The ethylacetate soluble part which contain again was then crystallized with MeOH to give yellow coloured crystals of aglycone, m.pt. 299°C. The aglycone gave a bathochromic shift of 14 nm in band II with NaOAc, thus showing that the sugar is linked at C–7 position.

Permethylation of I was followed by acid hydrolysis. CH_3I (1 ml) and Ag_2O (30 mg) were added to a solution of I (20 mg) in DMF (5 ml). The mixture was stirred in dark at R.T. for 48 hrs. The contents were filtered and the residue was washed with little DMF. The filtrate was evaporated to dryness and the residue was treated with ethanol (25 ml).

The syrupy residue was hydrolysed with 7% HCl. After usual work-up, it gave 7-OH, 3′,4′,5-trimethoxy flavone, m.pt. 185 °C. The methylated sugar was identified as 2,3,4,6-tetra-*O*-methyl-D-glucose.

ACKNOWLEDGEMENTS

The authors thank Principal Dr. A.K. Lahiry, and Head, Chemistry Department, Govt. Girls College, Bilaspur, for providing laboratory facilities and also the Director CDRI, Lucknow for spectral analyais.

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(*Received*: 15 January 1993; *Accepted*: 27 February 1993) AJC–589