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SHORT COMMUNICATION

PHYSCION 1-GLYCOSYL RHAMNOSIDE FROM SEEDS OF *DESMODIUM PULCHELLUM*

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Abstract—A new glycoside, the 1-glucosylrhamnoside of physcion has been identified in the seeds of *Desmodium pulchellum* (L).

Desmodium pulchellum (Leguminosae) is reputed for its medicinal importance[1] and Ghoshal and Mukherjee[2–4] isolated a number of alkaloids. Tiwari and co-workers[5] worked on the oil obtained from the seeds.

An anthraquinone glycoside, m.p. 220° was isolated from the water insoluble portion of the ethyl acetate extract of the seeds. The glycoside on acid hydrolysis gave an orange coloured aglycone, $C_{16}H_{12}O_5$ (m.p. 207°), D(+) glucose and L(−) rhamnose (paper chromatography and TLC). The colour reactions and spectral properties of the aglycone were like those of an anthraquinone. On the basis of standard colour reactions,[6–7] UV[8] and IR spectra[9] and other experiments the structure of the aglycone was assigned as 1,8-dihydroxy 6-methoxy-3-methyl anthraquinone, physcion. This structure was further confirmed by the study of the mass spectrometric fragmentation of the aglycone.

The position of the two sugars was determined by methylation technique which proved that they were present in the form of a bioside linked at 1-position of the aglycone. Partial hydrolysis gave glucose first showing rhamnose was linked to the aglycone. The non-reducing nature of the glycoside indicated that the reducing groups of both the sugars were involved in the glycosidic linkages. The glycoside isolated was unaffected by takadiastase but was completely hydrolysed by emulsin thereby showing both linkages to be β.

The glycoside was fully methylated and hydrolysed and the partially methylated sugars formed identified as β-2,3,4,6-tetra-*O*-methyl D-glucose and α-2,3 di-*O*-methyl L-rhamnose by paper chromatography. The disaccharide was thus 1-*O*-glycosyl (1 → 4) rhamnoside

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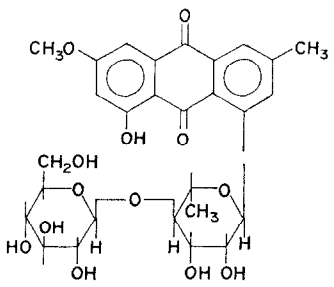
linked to the aglycone through the C-1 of the rhamnose. The result also confirmed the pyranose form of both sugars.

The nature of the disaccharide was confirmed by periodate oxidation; 1-mole of the glycoside consumed 3 moles of periodate with the formation of 1-mole of formic acid. This shows that three vicinal hydroxyl groups are free in glucose (two moles of periodate and formation of 1-mole of formic acid) whereas rhamnose contains only two vicinal free hydroxyl groups (1-mole of periodate). The structure of the glycoside has been shown to be (*I*).



I

EXPERIMENTAL

Isolation of the Glycoside

The defatted seeds of *Desmodium pulchellum* Linn. were extracted with EtOAc and the extract concentrated giving a resinous mass which was taken up in the min amount of EtOH. The EtOH was poured into ice H_2O and the brown residue was separated, washed (H_2O) and dried. It was refluxed with light petroleum, Et_2O and EtOAc successively. The EtOAc solution on concentration gave a brown precipitate which was crystallized from EtOAc–light petroleum giving pale yellow crystals m.p. 220° (decomposed) (C, 52 0; H, 5 00; Calc. for $C_{28}H_{32}O_{14}C$, 54 05; H, 5·40%). Mol. wt from HIO_4 oxidation = 536, Actual = 592.

Isolation of the Aglycone

The glycoside was hydrolysed using 4 N-H_2SO_4 and the aglycone extracted with Et_2O. The substance was crystallized from benzene–light petroleum giving orange coloured crystals m p. 207° (Found: C, 67·2, H, 4·8; OCH_3, 10 54. Calc. for $C_{16}H_{12}O_5$, C, 67 6; H, 4 22; OCH_3,10·92%; mol. wt. from mass spectrum, 284.) UV (EtOH): λ_{max} 289 and 436 nm. IR: Peaks identical with the reported values. Acetate: m p. 182–183°. (Found $COCH_3$, 22 14. Calc. for $C_{16}H_{10}O_5$ $(COCH_3)_2$ 23 37%.) The methyl ether (Me_2SO_4–K_2CO_3) was crystallized from MeOH, orange needles, m p. 121–122°. (Found: —OCH_3, 28 73. Calc. for $C_{15}H_7O_2$ $(OCH_3)_3$, 29·8%.) On oxidation with Cr_2O_3 it gave emodic acid trimethyl ether, m p. 270°, and with alkaline $KMnO_4$ 3:5-dimethoxy phthalic acid, m p. 158°.

Methylation of the Glycoside and Hydrolysis of the Methylated Product

The glycoside was methylated Me_2SO_4–NaOH giving a chocolate coloured methylated glycoside m.p. 225° (decomposed) It was hydrolysed with 4 N H_2SO_4 and the aglycone and partially methylated sugars were identified by paper chromatography

Hydrolysis with Emulsin

The glycoside dissolved in EtOH, was treated with aqueous solution emulsin from sweet almonds.[10] The mixture was kept at 37–40° for 4 days, the orange aglycone which precipitated was extracted with EtOAc and purified (m p. 199–200°). The remaining solution on paper chromatographic examination revealed the presence of glucose and rhamnose

Periodate oxidation

The glycoside was treated with $NaIO_4$ in aqueous ethanol at room temperature for 48 hr. The amount of IO_4 used and formic acid produced estimated by standard procedures.[11]

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