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A NEW ANTHRAQUINONE DIGALACTOSIDE FROM *CASSIA LAEVIGATA* PODS

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Key Word Index—*Cassia laevigata*; Leguminosae; pods; physcion 8-digalactoside; chrysophanol; anthraquinone pigments.

RESULTS

An anthraquinone, mp 196° was identified in the pods as chrysophanol by mp, mmp, IR and UV spectra [1]. An anthraquinone glycoside $C_{28}H_{32}O_{15}$, mp 152°(d) on acid hydrolysis gave an orange coloured aglycone $C_{15}H_{12}O_5$ mp 207° and D(+)-galactose (PC and osazone). The colour reactions and spectral properties of the aglycone were those of an anthraquinone; on the basis of colour reactions [2, 3], UV, IR, mass and NMR and other experiments the aglycone was identified as 1,8-dihydroxy-6-methoxy-3-methylanthraquinone (physcion).

Methylation of the glycoside with dimethylsulphate followed by acid hydrolysis gave 1,6-dimethoxy-8-hydroxy-3-methylanthraquinone (confirmed by mp and UV spectrum). This confirmed the attachment of sugar in position-8 of the aglycone. The glycoside was fully methylated, hydrolysed and the resulting partially methylated sugars were identified as 2,3,4,6-tetra-*O*-methylgalactose and 2,3,6-tri-*O*-methylgalactose by the method of Jones *et al.* [4] using 2,3,4,6-tetra-*O*-methylglucose [5] as standard. This established that two galactose units are present in the form of (1 → 4) bioside linked at position-8 of the aglycone. The nature of the (1 → 4) bioside was also confirmed by periodate oxidation; one mole of the glycoside consumed three moles of periodate with the liberation of one mole of formic acid. The glycoside was completely hydrolysed by emulsin thereby showing the presence of β-linkages. On this basis, the glycoside was identified as 1-hydroxy-6-methoxy-3-methylanthraquinone 8-*O*-β-D-galactosyl-(1 → 4)-*O*-β-D-galactopyranoside.

EXPERIMENTAL

Isolation and purification. The pods were extracted with EtOH and the extract was concd under red. pres. The conc extract was poured into H_2O and the coloured residue was extracted with petroleum, ether and concd. From the conc extract a yellow compound deposited which was crystallized from EtOAc–petrol. It had mp 196°, identified as chrysophanol. The petrol extracted residue was next extracted with C_6H_6. The C_6H_6 extract on concn gave a brown compound mp 152° (d), which was chromatographically homogenous. IR ν_{max}^{KBr} cm^{-1}: 3310, 3060, 2858, 1740, 1680, 1640, 1615, 1592, 1470, 1450, 1380, 1365, 1300, 1290, 1225, 1210, 1170, 1100, 1035, 990, 900, 890, 860, 830 and 770. λ_{max}^{EtOH} nm: 266, 290 and 412. NMR (60 Hz, $CDCl_3$) δ: 7.18 (*s*, 1-H, C-2); 7.92 (*s*, 1-H, C-4) 7.40 (*d*, 1-H, C-5); 6.92 (*d*, 1-H, C-7) 4.00 (*s*, 3H, —OCH_3); 2.52 (3H, C—CH_3) 3.52 (10-H, sugar protons) and 5.62 (H-1 galactosyl). MS *m/e* 608 (M^+) (Found: C, 55.20; H, 5.34. Calcd. for $C_{28}H_{32}O_{15}$: C, 55.26; H, 5.26%).

Methylation of the glycoside and hydrolysis of the methylated product. The glycoside was methylated with Me_2SO_4 in aq. NaOH giving methylated glycoside mp 120° (d). It was hydrolysed with 4N H_2SO_4. The partially methylated sugars were identified by PC in *n*-BuOH–EtOH–H_2O (5:1:4). Methylated galactose were identified by the method of Jones *et al.* [4]. In this method 2,3,4,6-tetra-*O*-glucose was used as standard and the partially methylated sugars were identified by their relative R_fs.

Hydrolysis with emulsion. The glycoside dissolved in EtOH and an aq. soln of emulsin from sweet almonds [6] was left at 40° for 48 hr. The orange aglycone which precipitated was extracted with EtOAc. The remaining soln on PC revealed the presence of galactose.

Periodate oxidation. The glycoside was treated with $NaIO_4$ in aq. EtOH at room temp. for 48 hr. The amount of periodate used and formic acid produced was estimated by standard procedures [7].

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