Indian Journal of Chemistry
Vol. 38B, September 1999 , pp. 1143 - 1144

Note

Xanthone Glycoside from rhizome of *Acorus calamus*

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Received 15 May 1997; accepted 6 June 1998

Chemical investigation of the rhizome of *Acorus calamus* yields a new xanthone glycoside designated as 4,5,8-terimethoxy-xanthone- 2 -*O*-β-D-glucopyranosyl(1→2)-*O*-β-D-galactopyranoside **1**. The structure of this glycoside has been established on the basis of chemical and spectral evidences.

The rhizome of *Acorus calamus* Linn. (Fam. Araceae), commonly known as "Butch" is a useful medicinal plant found throughout India, Ceylon and Sikkim. In India it is mostly found in marshy tracts of Kashmir and Sirmon in Manipur, and Nagahills[1]. Its rhizome has medicinal properties against bed bugs, moths, lice, emetic stomach in dyspep etc.[2].

The new xanthone glycoside was isolated as described in Experimental Section, mp 270 °C. It analysed for $C_{28}H_{36}O_{16}$ and on hydrolysis with 7% H_2SO_4 gave galactose and glucose (PC) as sugar moieties and an aglycone which was shown to be a xanthone by its colour reactions and UV spectral data[3].

The aglycone, $C_{16}H_{14}O_6$, mp 257 °C, showed characteristic colour reactions of xanthone. In ^{1}H NMR spectrum four aromatic protons (*meta* and *ortho* coupled) appeared at δ 6.38 (1H, d, *J*=3.0 Hz), 6.52 (1H,d *J*=3.0 Hz), 6.73 (1H, d *J*=10 Hz), 7.20 (1H,d *J*=10 Hz). In addition, two singlets corresponding to three protons and six protons appeared at δ 3.87 (3H, s) and δ 3.97 (6H, s) due to three methoxy groups (-OCH_3) in which two methoxyl groups were in identical environment. The appearance of four aromatic protons as four different (*ortho-meta*) split doublets were indicative of four oxygen functions (three-OCH_3 and one-OH) distributed in both rings.

Complete acetylation of aglycone with AC_2O in pyridine yielded a monoacetyl derivative showing the presence of one hydroxyl group with three methoxy groups. In ^{1}H NMR spectrum of the acetylated aglycone the downfield shift of *meta*-coupled aromatic protons (δ 6.50 1H,d *J*=3.0 Hz and δ 6.90 1H, d *J*=3.0 Hz) indicated the presence of acetylated hydroxyl group and *meta*-coupled protons in the same ring. The aglycone did not show a bathochromic shift with $AlCl_3$ in UV spectrum indicating the absence of perihydroxyl group, i.e. at C-1, C-8. This shows that hydroxyl group is present at C-2. Absence of C-8 carbonyl deshielded protons indicates that the aglycone was oxygenated at C-8 position.

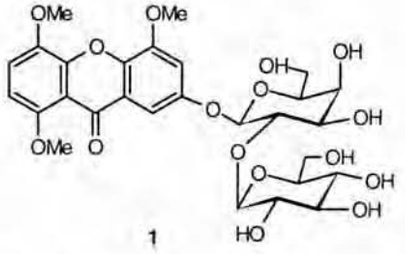
Further, ^{1}H NMR spectrum of the compound showed the presence of three -OCH_3 groups at C-4, C-5 and C-8 δ 3.97 (6H, s for C-4 & C-5) and δ 3.86 (3H, s for C-8) respectively.

The glycoside gave positive Molisch's test[4] but neither reduced Fehling's solution nor gave positive colour test with AHP reagent[5] suggesting the involvement of reducing group in sugar linkage. Thus, sugar moiety was attached at C-2. Such as attachment was also confirmed by positive test with Gibb's reagent.

The glycoside showed two anomeric protons at δ 5.78 (1H,d) and δ 4.90 (1H, d) for glucose and galactose, respectively. Enzymatic hydrolysis with β-glucosi-dase confirmed the presence of sugar moieties as bioside and that galactose was directly attached to aglycone with C-O-C linkage and glucose was the external sugar unit.

The glycoside was completely methylated, hydrolysed and the resulting partially methylated sugars were identified as 3,4,6-tri-*O*-methyl-D-galactose and 2,3,4,6-tetra-*O*-methyl-D-glucose. This established that the two sugar units were present in the form of (1→2) bioside.

Based on the chemical and spectral evidences, the compound has been assigned the structure as 4,5,8-trimethoxyxanthone-2-O-β-D-glucopyranosyl(1→2)-*O*-β-D-galactopyranoside **1.**



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Experimental Section

The plant *Acorus calamus* was collelcted from Jabalpur (MP), India. A herbarium specimen is in file

in BSI, Allahabad (sheet no. 18881). Melting points are uncorrected. IR spectra were run in KBr on a Perkin-Elmer spectrophotometer, and ^{1}H NMR spectra were recorded at 200 MHz in $CDCl_3$ in FT mode.

Extraction and isolation of the compound. The air-dried and crushed rhizome (3 kg) was extracted with boiling ethanol, and the extracted concentrated under reduced pressure. It was separated by column chromatography on silica gel 60 (Merck 24398) using different organic solvents of increasing polarity. The glycoside was obtained from benzene-DCM (9:1 v/v) fraction and crystallised from ethyl acetate at 10 °C, mp 270 °C; R_f 0.51 (ethyl acetate-methanol; 7:3 v/v); UV (MeOH): 220, 240, 255, 265, 360 nm; IR: 1635, 1620, 1575 cm^{-1}; ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.5-3.85(12H, br s, sugar protons), 3.86 (3H, s, -OCH_3), 3.97 (6H, s, 2x-OCH_3) 6.38 (1H, d, *J*=3.0 Hz) 6.52 (1H, d, *J*=3.0 Hz), 6.73 (1H, d *J*=10 Hz), 7.20 (1H, d, *J*=10 Hz), 4.90 (1H, d, *J*=5.2 Hz, H-1" galactosyl) 5.78 (1H, d, *J*=7.5 Hz, H-1" glucosyl).

Acid hydrolysis with 7% H_2SO_4 gave an aglycone (Found: C: 63.0%; H: 4.61%. Calcd for $C_{16}H_{14}O_6$ C:63.58% H: 4.64% and two sugar moieties identified as D-glucose and D-galactose (cochromatography with an authentic sample).

References

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