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GLYCOSYLXANTHONES FROM ACORUS CALAMUS

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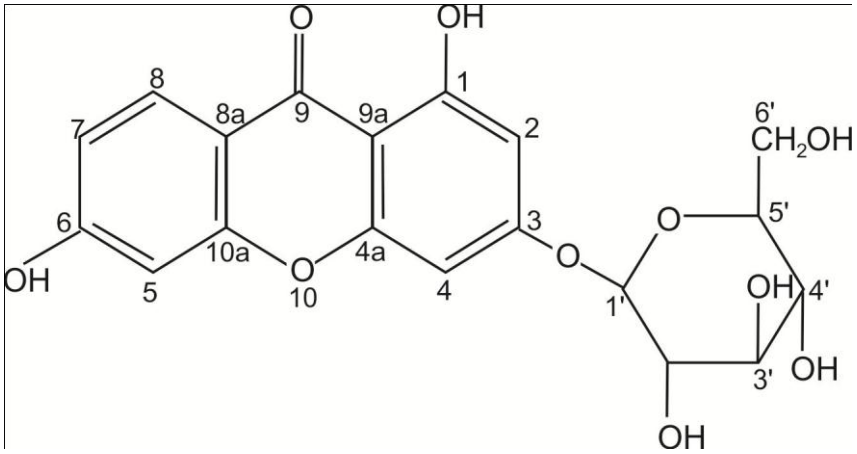
Two new xanthone glycoside, 3-O-β-D-glucopyranosyl-1.6-dihydroxy xanthone **1** and 3-C-β-D-glucopyranosyl-1-hydroxy-7-methoxyxanthone **2** have been isolated from the rihzome of *Acorus calamus*. Their structures have been established by spectroscopic studies (FABMS, HNMR, CNMR, DEPT and COSY) and by comparison with closely related compounds. *Acorus calamus* belongs to the family Araceae. It grows in India,[1] Ceylon and Sikkim. Its rhizome has medicinal properties against bed bugs, mouth, lice, emetic stomach in dyspep etc.[2] Here we report the isolation and structural elucidation of two new O-and C-Glycosylxanthones named as 3-O-β-D-glucopyranosyl-1.6-dihydroxyxanthone **1** and 3-C-β-D-glucopyranosyl-1-hydroxy-7-methoxy-xanthone **2**.

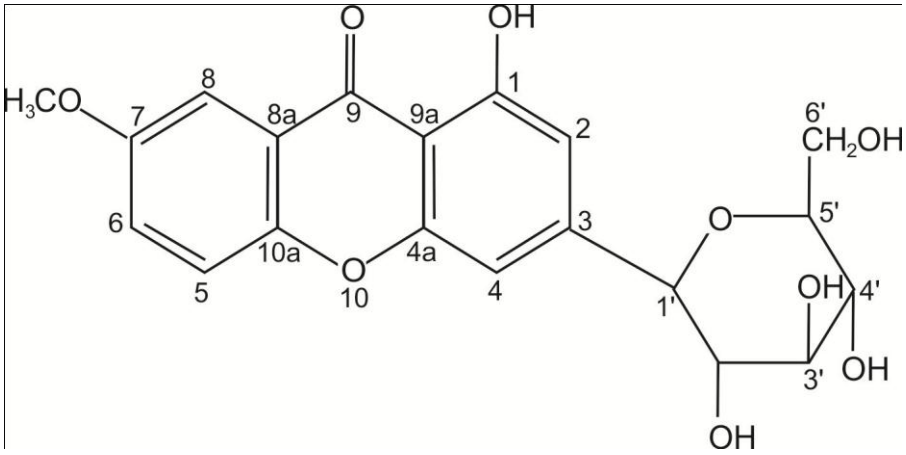
RESULT AND DISCUSSION

Compound **1** was assigned the molecular formula $C_{19}H_{18}O_{10}$ on the basis of ^{I}H and ^{13}C NMR, DEPT and FAB mass spectrum. Its FAB mass spectrum exhibited a molecular ion peak at m/z 406. Combined with ^{I}H NMR δ 5.06 (d, 1H, J=7.5 Hz). 3.00-4.00 (m, glu-H) and ^{13}C NMR (δ 99.9, 73.1, 77.1, 69.5, 76.4, 60.6) data indicated the presence of an O-linked β-D-glucopyranosyl moiety. In the ^{I}H NMR δ 12.96, s; 10.42, s; 6.44, s; 6.83, s; 6.87, s; 6.93, d (J=8.5Hz), 7.95, d (J=8.5 Hz) and ^{13}C NMR spectrum the remaining thirteen carbon signals (δ 161.6, 99.2, 162.9, 94.9, 164.2, 156.9, 103.1, 161.3, 116.0, 128.6, 121.0, 105.3, 182.0) were similar to those of the dihydroxyxanthone moiety of O-β-D-glucopyranosyl[3-4]. Its IR spectrum shows absorption bands at 3400-3100, 1600-1400, 1100-1040 and 890-900 indicative of ketone group, hydroxy functions and a β-D-glucoside moiety. Consequently, the structure 1 was established as β-D-glucopyranosyl-1.6-dihydroxy xanthone, which was confirmed by the HMQC and HMBC spectrum experiments. In the HMBC spectrum of 1, the long range coupling of C-1 and C-6 with hydroxyl group proton (δ 12.96, 10.42) located the hydroxy group at C-1 and C-6 respectively. As well as the long range coupling of C-3 with

sugar moiety end-group proton (H-1') suggested that the sugar moiety was at C-3. The correlation between C-2 and H-2, C-4 and H-4, C-5 and H-5, C-7 and H-7, C-8 and H-8 in the HMQC suggested a 3-O-β-D-glucopyranosyl-1.6-dihydroxy xanthone presence. (See table 1).



Compound-1



Compound-2

The ^{I}H, ^{13}C NMR, DEPT (Table 1 and 2) along with the IR spectrum of compound **2** were very close to those of **1** except for the presence of a methoxyl and the high field shifted of C-1'. The molecular formula $C_{20}H_{20}O_9$, was deduced from its MS and NMR spectra. The long range coupling of C-1 with hydroxyl group proton (δ=13.5) as well as C-7 with methoxy proton (δ=3.90) observed in the HMBC of 2 (Table 2) suggested that the hydroxyl group was at C-1 and the methoxyl group way at The highfield shifted of C-1' (Table 2) indicated the presence of a C-linked β-D-glucopyranosyl moiety[5-6], which was confirmed by the fragment ion of FABMS: m/z 163(100). In the HMBC spectrum the long range coupling of C-3 with

H-1' (δ=4.59) located the β-D-glucopyranosyl moiety at C-3. Compound **2** was therefore, assigned as 3-C-β-D-glucopyranosyl-l-hydroxy-7-methoxyxanthone.

Experimental Section

The plant *Acorus calamus* was collected from Jabalpur (M.P.), India.Melting points were uncorrected. IR spectra were taken on a Parkin Elmer FT-IR spectrometer. ^{I}H NMR, ^{13}C NMR and 2D NMR spectra were recorded on a Bruker AM 400FT-NMR spectrometer using TMS as internal standard. FAB-MS were obtained on a VG-ZAB-HS and VG-Auto Spec-3000 Mass spectrometer. Silica gel (200-300 mesh) was used for CC and silica GF_{154}(10-40u)for TLC. Spots were detected on TLC under UV lamp or by heating after spraying with 5% H_2SO_4.

Extraction and Isolation

Dry rhizome of *Acorus calamus* (900gm) was immersed in 95% alcohol for 30 days. The gum (34g) obtained after concentrating the exact, was then extracted with EtOAc, the extract was concentrated and the residue chromatographed on a silica gel column eluted with a gradient of $CHCl_3$ and MeOH. The fraction eluted with $CHCl_3$-MeOH(3:1) was rechromatographed on a silica gel column several times, eluting with $CHCl_3$- MeOH to yield compound 1 (10mg) and 2 (20mg).

3-O-β-D-glucopyranosyl-1.6-dibydroxyxanthone (1) White needles (MeOH). m.p.236-240 °C ,IR: 3350,2950,2850,1662 1630,1603,1490,1320,1230,1072,1040,1023,895,811. FABMS, m/z: 406(M^+ $C_{19}H_{18}O_{10}$),^{I}H NMR [400MHz, $(CD_3)_2SO_4$TMS], δ ppm: 12.96(1H, s, 1-OH), 12.42(1H,s,6.OH), 6.44(1H, s, H-2), 6.83(1H, s, H-4), 6.87(1H, s, H-5), 6.93(1H, d J=8.5Hz, H-7), 7.95(1H, d, J=8.5 Hz, H-8), 5.06(1H, d, J=7.5Hz, H-1'), 3.00-4.00(m, glu-H), ^{13}C NMR [100MHz, $(CD_3)_2SO$, TMS]. δ ppm: 161.1(C-4), 99.5(C-2), 162.9(C-3), 94.8(C-4), 164.2(C-4a). 156.9(C-10a), 103.1(C-5), 161.3(C-6), 116.0(C-7), 128.6(C-8), 121.0(C-8a).105.3(C-9a), 182.0(>C=0), 99.9(C-1'), 76.1(C-2'), 77.1(C-3'), 69.5(C-4'), 76.4(C-5'), 60.6(C-6'), ^{I}H and ^{13}C NMR Chemical shift assignments and HMQC, HMBC correlations see Table 1.

3-C- β--D-glucopyranosyl-l-hydroxy-7-methoxyxanthone (2) Yellow crystals (MeOH), m.p. 198-200°C, IR: 3360, 1660, 1605, 1488, 1349, 1230, 1074, 1035, 1015, 833. FABMS m/z 404 (M^+ $C_{20}H_{20}O_9$) 163 (M^+–$C_{I4}H_9O_5$, 100), ^{I}HNMR [400 MHz $(CD_3)_2SO$, TMS]δppm:13.57(1H, s,1-OH), 6.91(1H,s, 1-H-2), 6.54(1H,s, H-4), 6.94(1H,d, J=8.4Hz, H-5), 7.58(1H, d, J=9.0Hz, H-6), 7.56(H, s, H-8), 3.90 (3H,s,-OCH_3),4.59(1H, d, J=9, 8Hz, H-

1'), 3.00-4.00 (m,glu-H), ^{13}C NMR[100MHz, $(CD_3)_2SO$, TMS],δppm: 160.6 (C-1), 103.2(C-2), 163.4(C-3), 9.37(C-4), 156.2(C-4a), 154.7(C-10a), 115.8(C-5), 120.3(C-6), 148.0(C-7), 110.2(C-8), 121.4(C-8a), 108.8(C-9a), 182.0(>C=O), 56.0(-OCH_3), 73.25(C-1'), 70.5(C-2'). 78.9(C-3'), 70.2(C-4'), 81.5(C-5'), 61.4(C-6'), ^{I}H and ^{13}C Chemical shift assignments and HMQC, HMBC correlations see Table 2.

Table 1: ^{I}H NMR (400MHz) and ^{13}C NMR (100 MHz) data and HMBC correlations of 1 in ppm).

1-OH	12.96(s)	1	161.1 s	H-2, 1-OH
2	6.44(s)	2	99.5 d	H-2, I –OH
		3	162.9 s	H-2, H-4, H-1’
4	6.83(s)	4	94.8 d	H-2, H-4
		4a	156.9 s	H-4
		10a	164.2 s	H-5, H-8
5	6.87(s)	5	103.1 d	H-5
6-OH	10.42(s)	6	161.3s	H-5, H-7, H-8, 6-OH
7	6.93(d, J=8.5Hz)	7	116.0d	H-5, H-7, H-8, 6-OH
8	7.95(d, J=8.5Hz)	8	128.6 d	H-7, H-8
		8a	121.0 s	H-5, H-7, H-8
		9a	105.3 s	H-2
		9	182.0 s	
Glc-1'	5.06(d, J=7.5Hz)	1'	99.9 d	
Glc-2'-6'	3.00-4.00(m)	2'	73.1 d	1’-H
		3'	77.1 d	1'-H
		4'	68.5 d	
		5'	76.4 d	1’-H
		6'	60.6 t	

* Multiplicities were determined by DEPT.

Table II: IH NMR (400MHz) and ^{13}C NMR (100 MHz) data and HMBC correlations of 2 in DMSO-d_6 (δ in ppm).

H	δ_H	C	δ_c*	1H-^{13}C long range correlation
1-OH	13.57(s)	1	160.6 s	H-2, 1-OH
2	6.91(s)	2	103.2 d	H-2, H-4, 1-OH
		3	163.4 s	H-2, H-4, H-1
4	6.54(s)	4	93.7 d	H-4
		4a	156.2 s	H-4
		10a	150.7 s	H-5, H-6
5	6.94(d, J=8.4Hz)	5	115.8 d	H-5
6	7.58(d, J=9.0Hz)	6	120.3 d	H-5, H-8
		7	148.0 s	H-6, H-8
8	7.56(s)	8	110.2d	H-6
		8a	121.4 s	H-5, H-8
		9a	108.8 s	H-4, H-8
		9	182.0 s	
OCH_3	3.90(s)	OCH_3	56.0 q	
Glc-1'	4.59(d, J=9.8Hz)	1'	73.25 d	
Glc-2'-6'	3.00-4.00(m)	2'	70.6 d	H-1'
		3'	78.9 d	H-1'
		4'	70.2 d	
		5'	81.5d	H-1'
		6'	61.4t	

* Multiplicities were determined by DEPT.

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