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Note

Two new O- and C-glycosylxanthones from *Gentiana tizuensis* Franch[†]

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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 aerial parts of *Gentiane tizuensis*. Their structures have been established by spectroscopic studies (FABMS, ^{1}H NMR, ^{13}C NMR, DEPT and COSY) and by comparison with closely related compounds.

Gentiana tizuensis Franch belongs to the tribe Gentiana. It grows in the northwest of China and is used in traditional folk medicine for the treatment of hepatitis[1]. We reported the four known chemical components from *Gentiana tizuensis* Franch[2]. In this note, we wish to report the isolation and structural elucidation of two new O-and C-Glycosylxanthones named as 3-*O*-β-D-glucopyranosyl-1.6-dihydroxy-xanthone **1** and 3-*C*-β-D-glucopyranosyl-1-hydroxy-7-methoxyxanthone **2**.

Results and Discussion

Compound **1** was assigned the molecular formula $C_{19}H_{18}O_{10}$ on the basis of ^{1}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 ^{1}H NMR δ5.06 (d, 1H, *J*=7.5Hz), 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 ^{1}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*=8.5Hz) and ^{13}C NMR spectrum the remaining thirteen carbon signals (δ 161.6, 99.5, 162.9, 94.8, 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 3-*O*-β-D - glu-copyranosyl-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 I**). Compound **1** undergoes smooth hydrolysis to furnish the aglycon, which is a yellowish powder, and an aqueous phase. Sugar part of the molecule is identified as D-glucose from the aqueous phase by comparing with authentic sample(PC).

The ^{1}H, ^{13}C NMR, DEPT (**Tables I** and **II**) along with the IR spectrum of compound **2** were very close to those of **1** except for the presence of a methoxyl and the highfield 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 II**) suggested that the hydroxyl group was at C-1 and the methoxyl group was at C-7. The highfield shifted of C-1′in ^{13}C NMR spectrum (**Table II**) 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. Therefore compound **2** was assigned as 3-*C*-β-D-glucopyranosyl-1-hydroxy-7-methoxyxanthone (**Figure 1**)

Experimental Section

Melting points were recorded on a Kofler melting point apparatus and were uncorrected. IR spectra were

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Table I —^{1}H NMR (400MHz) and ^{13}C NMR (100 MHz) data and HMQC, HMBC correlations of **1** in DMSO-d_6 (δ in ppm)

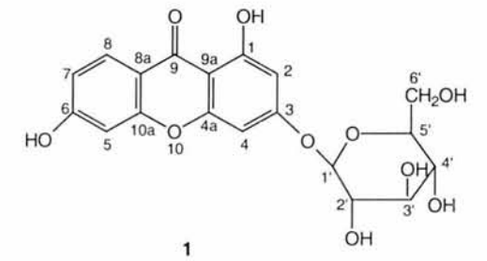
C	δ_c*	H	δ_H	HMQC(C→H)	HMBC(C→H)
1	161.1s	1-OH	12.96(s)		H-2, 1-OH
2	99.5d	2	6.44(s)	H-2	H-2, 1-OH
3	162.9s				H-2, H-4, H-1′
4	94.8d	4	6.83(s)	H-4	H-2, H-4
4a	156.9s				H-4
10a	164.2s				H-5, H-8
5	103.1d	5	6.87(s)	H-5	H-5
6	161.3s	6-OH	10.42(s)		H-5, H-7, H-8, 6-OH
7	116.0d	7	6.93(d, *J*=8.5Hz)	H-7	H-5, H-7, H-8, 6-OH
8	128.6d	8	7.95(d, *J*=8.5Hz)	H-8	H-7, H-8
8a	121.0s				H-5, H-7, H-8
9a	105.3s				H-2
9	182.0s				
1′	99.9d		glc-1′5.06(d, =7.5Hz)	glc-H-1′	glc-H-2′
2′	73.1d		glc-2′-6′3.00-4.00(m)	glc-H-2′	glc-H-1′, 3′
3′	77.1d			glc-H-3′	glc-H-2′, 4′, 1′
4′	68.5d			glc-H-4′	glc-H-3′, 5′
5′	76.4d			glc-H-5′	glc-H-4′, 6′, 1′
6′	60.6t			glc-H-6′	glc-H-5′

* Multiplicities were determined by DEPT and HMQC.

Table II—^{1}H NMR (400MHz) and ^{13}C NMR (100 MHz) data and HMQC, HMBC correlations of **2** in DMSO-d_6 (δ in ppm)

C	δ_c*	H	δ_H	HMQC(C→H)	HMBC(C→H)
1	160.6s	1-OH	13.57(s)		H-2, 1-OH
2	103.2d	2	6.91(s)	H-2	H-2, H-4, 1-OH
3	163.4s				H-2, H-4, H-1′
4	93.7d	4	6.54(s)	H-4	H-4
4a	156.2s				H-4
10a	150.7s				H-5, H-6
5	115.8d	5	6.94(d, *J*=8.4Hz)	H-5	H-5
6	120.3d	6	7.58(d, *J*=9.0Hz)	H-6	H-5, H-8
7	148.0s			H-6, H-8	
8	110.2d	8	7.56(s)	H-8	H-6
8a	121.4s				H-5, H-8
9a	108.8s				H-4, H-8
9	182.0s				
OCH_3	56.0q	OCH_3	3.90(s)	H-OCH_3	
1′	73.25d	glc-1′	4.59(d, *J*=9.8Hz)	glc-H-1′	glc-H-2′
2′	70.6d	glc-2′-6′	3.00-4.00(m)	glc-H-2′	glc-H-1′, 3′
3′	78.9d			glc-H-3′	glc-H-2′, 4′
4′	70.2d			glc-H-4′	glc-H-3′, 5′
5′	81.5d			glc-H-5′	glc-H-4′, 6′, 1′
6′	61.4t			glc-H-6′	glc-H-5′

* Multiplicities were determined by DEPT and HMQC.



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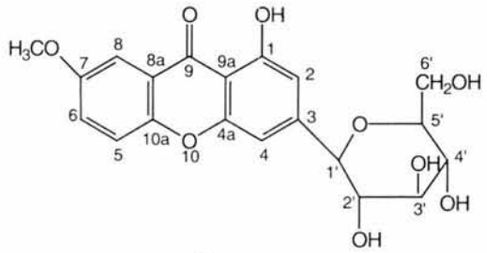

2

Figure 1

taken on a Nicolet 170SX FT-IR spectrometer. ^{1}H NMR, ^{13}C NMR and 2D NMR spectra were recorded on a Bruker AM 400FT-NMR spectrometer using TMS as internal standard. FABMS 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_{254}(10-40u)for TLC. Spots were detected on TLC under UV lamp or by heating after spraying with 5% H_2SO_4.

Plant material. *Gentiana Tizuensis* Franch was collected from Guo luo Huashixia mountain (an altitude of 4100 meters above sea level), QingHai province, China in July 1995 and identified by Senior Engineer Run-de Zhen(Northwest platean Institute of Botanu, Academia Simica, Xining 81001).

Extraction and isolation. Dry leaves and branches of *G. tizuensis* (650g) were immersed in 95% alcohol for 30 days. The gum (34g) obtained after concentrating the exact, was then extracted with EtOAc, the extract was concd. 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-dihydroxyxanthone 1: White needles (MeOH). m.p.236-40°C; IR: 3350, 2930, 2850, 1662, 1630, 1603, 1490, 1320, 1072, 1040, 1023, 895, 811; FABMS, m/z: 406(M^+, $C_{19}H_{18}O_{10}$); ^{1}H NMR [400MHz. $(CD_3)_2SO$, TMS]: δ 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*=8.5Hz, H-8), 5.06(1H, d, *J*=7.5Hz, H-1′), 3.00-4.00(m, glu-H); ^{13}C NMR [400MHz, $(CD_3)_2SO$, TMS]: δ 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=O), 99.9(C-1′), 76.1(C-2′), 77.1(C-3′), 69.5(C-4′), 76.4(C-5′), 60.6(C-6′). For ^{1}H and ^{13}C NMR chemical shift assignments and HMQC, HMBC correlations see **Table I**.

Glycoside 1 (8 mg) was heated on a water bath (60°C) with 2*M*HCl in 50% EtOH solution(*p*H=1) for 1hr. The yellowish powder was precipitated and filtered. The sugar part of the molecule was identified as D-glucose from the aqueous phase by comparing with D-glucose sample (PC). The Rf value is 0.26 in nC_4H_9OH-AcOH- H_2O(4:1:5) system.

3-*C*-β-D-glucopyranosyl-1-hydroxy-7-methoxyxanthone 2. Yellow crystals (MeOH), m.p. 198-200°C; IR: 3350, 1650, 1605, 1488, 1349, 1230, 1074, 1035, 1015, 833; FABMS, m/z: 404 (M^+ $C_{20}H_{20}O_9$) 163(M^+-$C_{14}H_9O_4$, 100); ^{1}H NMR[400 MHz $(CD_3)_2SO$, TMS]: δ 13.57(1H, s, 1-OH), 6.91(1H, s, 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(1H, 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[400MHz, $(CD_3)_2SO$, TMS]: δ 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′). For ^{1}H and ^{13}C chemical shift assignments and HMQC, HMBC correlations see **Table II.**

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