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Two New Xanthone Glycosides from *Securidaca inappendiculata*

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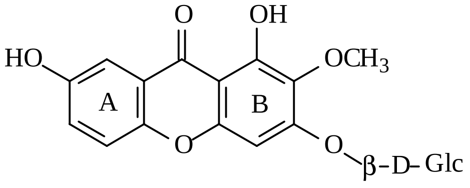
Abstract: Two new xanthone glycosides, securixanside B and C, were isolated from the stems of *Securidaca inappendiculata.* Their structures were determined as 3-O-β-D-glucopyranosyl-1,7-dihydroxy-2-methoxyxanthone and 6-O-β-D-glucopyranosyl-1-hydroxy-4,7-dimethoxyxanthone by spectroscopic methods.

Keywords: *Securidaca inappendiculata*, xanthone glycoside, securixanside B and C.

Securidaca inappendiculata Hassk. is liana which distributed in the south of China. It is used in Guangxi folk medicine for the treatment of rheumatalgia, enterogastritis and inflammatory disease[1]. We report here the structure elucidation of two new xanthone glycosides, 3-O-β-D-gluco-pyranosyl-1,7-dihydroxy-2-methoxyxanthone (**1**) and 6-O-β-D-glucopyranosyl-1-hydroxy-4,7-dimethoxyxanthone (**2**), isolated from the stems of *S. inappendiculata.*



1

Compound **1** was obtained as yellow amorphous solid, mp 256℃. The FAB mass spectrum displayed a quasi-molecular ion peak at *m/z* 437 $[M+H]^+$ and a prominent fragment ion peak at *m/z* 275 $[M+H-162]^+$ due to the loss of sugar moiety. In combination with the NMR spectral data (**Table 1**), the molecular formula of **1** was determined to be $C_{20}H_{20}O_{11}$. The ^1H, ^{13}C NMR spectra showed signals for a glucose unit, which was confirmed by TLC after acid hydrolysis of **1**[4]. The UV absorption bands at 234, 256, 294, 374 nm and IR (KBr) absorption bands at 3440, 1660, 1600 and 1575 cm^{-1} suggested the presence of xanthone skeleton. The signal at δ 12.73 ppm in

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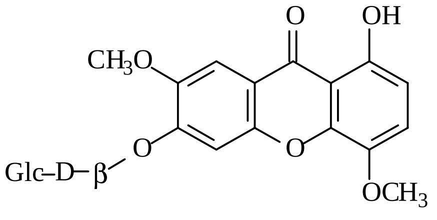
^{1}H NMR spectrum of **1** (DMSO-d_6) indicated that a hydroxyl was chelated to a carbonyl group[2]. The ^{1}H NMR spectrum also exhibited one aromatic proton at δ 6.85 ppm (s), and three coupled aromatic protons at δ 7.33 (dd, J = 9.0, 3.0Hz), δ 7.50 (d, J = 9.0 Hz) and δ 7.45 (d, J = 3.0Hz), indicating that A ring was mono-substituted and B ring was tri-substituted. The signals of the anomeric proton of the glucose appeared at δ 5.14 (d, J = 7.1 Hz) in the ^{1}H NMR spectrum, indicating that the sugar moiety should be β-orientated. Comparison of the ^{1}H, ^{13}C NMR and EIMS spectral data of **1** with the known compound, 1, 3, 7-trihydroxy-2-methoxyxanthone[3], showed that the aglycone of **1** was 1, 3, 7-trihydroxy-2-methoxyxanthone and β-glucose was connected at C-3 position. Therefore, **1** was identified as 3-O-β-D-glucopyranosyl-1,7-dihydroxy-2-methoxyxanthone, named securixanside B.

Table 1 ^{13}C NMR (125 MHz) and ^{1}H NMR (500 MHz) data of **1** (DMSO-d_6, TMS, δ, ppm)

No.	^{13}C	^{1}H	No.	^{13}C	^{1}H
1	153.3		8b	103.5	
2	131.5		C=O	180.5	
3	153.5		Glc-1′	100.1	5.14 d (7.1)
4	93.7	6.85 s	2′	73.1	
4a	152.2		3′	76.5	
4b	149.1		4′	69.6	
5	118.7	7.50 d (9.0)	5′	77.1	
6	124.7	7.33 dd (9.0, 3.0)	6′	60.6	
7	153.8		MeO-2	60.2	3.87 s
8	107.7	7.45 d (3.0)	HO-1		12.73 s
8a	119.8		HO-7		9.85 s

Coupling constants (Hz) in parentheses.

Compound **2** was obtained as yellow amorphous solid, mp 276°C. Its HR FABMS showed a quasi-molecular ion peak at *m/z* 451.1241 $[M+H]^+$, calculated 451.1240 for $C_{21}H_{22}O_{11}$. The FABMS displayed a prominent fragment ion peak at *m/z* 289 $[M+H-162]^+$ due to the loss of hexose moiety. The ^{1}H, ^{13}C NMR spectra showed signals for a glucose unit, which was confirmed by TLC after acid hydrolysis of **2**[4].



2

The UV spectrum of **2** exhibited characteristic absorption bands of a xanthone (λ_{max}^{MeOH} 226, 266, 310, 378 nm). The presence of a free hydroxyl group at C-6 or C-3 were excluded based on the lack of any change in the UV spectrum with NaOAc[5]. The ^{1}H NMR spectrum displayed signals of two aromatic methoxyl (δ 3.84, 3.89), an AB system of two protons ortho-coupled (δ 7.51 and 7.03; J = 9.0Hz) and two singlets (δ

7.51, 7.31), indicating that one aromatic ring was 2,3-ortho-disubstituted and the other was 1,4-para-disubstituted. The signal at δ 12.87ppm in ^{1}H NMR spectrum of **2** indicated that a hydroxyl was chelated to a carbonyl group[6]. The presence of 6-O-β-D-glucopyranosyl-7-methoxyl and 1-hydroxy-4-methoxyl aromatic ring moiety in **2** was supported by comparison of the ^{13}C and ^{1}H NMR spectrum of **2** with known compounds, 6-O-β-D-glucopyranosyl-1-hydroxy-7-methoxyxanthone (**3**)[7] and 1,7-di-hydroxy-4-methoxyxanthone (**4**)[8]. The shifts of corresponding carbons in the ^{13}C NMR spectrum of **2**, **3** and **4** are essentially the same (**Table 2**). The signals of the anomeric proton of the glucose appeared at δ 5.05 (d, J = 6.0 Hz) in the ^{1}H NMR spectrum, indicating that the sugar moiety should be β-orientated.

From above chemical and spectral evidences, the compound was identified as 6-O-β-D-glucopyranosyl-1-hydroxy-4,7-dimethoxyxanthone, named securixanside C.

Table 2 ^{13}C NMR and ^{1}H NMR data of **2** (125/500 MHz), **3** (100/400 MHz) and **4** (75/300 MHz) (DMSO-d_6, TMS, δ, ppm)

No.	**2**		**3**[a]		**4**[b]	
	δ C	δ H	δ C	δ H	δ C	δ H
1	154.0		160.8		153.3	
2	108.1	7.03 d (9.0)	109.9	6.80 dd (8.3, 1.0)	108.0	6.71 d (8.9)
3	121.4	7.51 d (9.0)	136.6	7.69 t (8.3)	120.1	7.45 d (9)
4	142.1		107.4	7.06 dd (8.3, 1.0)	139.9	
4a	149.7		155.8			
4b	149.4		146.9		154.3	
5	103.1	7.31 s	103.1	7.36 s	119.7	7.59 d (9)
6	152.2		153.8		125.8	7.36 dd (9, 2.8)
7	146.8		146.9		145.2	
8	104.7	7.51 s	104.6	7.54 s	107.8	7.44 d (2.6)
8a	122.8		113.3		120.5	
8b	105.6					
C=O	180.9		180.4		181.7	
Glc-1′	99.7	5.05 d (6.0)	99.5	5.24 d (7.3)		
2′	73.1		73.0			
3′	76.7		76.6			
4′	69.6		69.4			
5′	77.2		77.1			
6′	60.7		60.6			
HO-1		12.87 s		12.79 s		11.99 s
HO-7						10.19 brs
MeO-4	56.8	3.84 s				3.88 s
MeO-7	56.0	3.89 s	55.9	3.91	56.8	

Coupling constants (Hz) in parentheses.

a) Data from reference 7.
b) Data from reference 8.

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