Chinese Chemical Letters Vol. 13, No. 8, pp 748 – 751, 2002
http://www.imm.ac.cn/journal/ccl/html

Two New Chromone Glycosides from *Selaginella uncinata*

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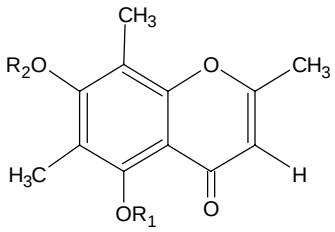
Abstract: Two new chromone glycosides, 5-hydroxy-2,6,8-trimethylchromon-7-O-β-D-gluco-pyranoside, named uncinoside A; 5-acetoxy-2,6,8-trimethylchromone-7-O-β-D-glucopyranoside, named uncinoside B, and a known chromone compound named 8-methyl eugenitol were isolated from *Selaginella uncinata.* Their structures were elucidated by spectra analysis of FAB-MS, 1D NMR and 2D NMR including ^{1}H NMR, ^{13}C NMR, HMQC, HMBC and single-crystal X-ray diffraction techniques.

Keywords: *Selaginella uncinata,* chromone glycosides, uncinoside A, uncinoside B.

Selaginella uncinata (Desv.) Spring is a Chinese herbal medicine widely distributed in south China, which has been used to treat bacterial diseases, infectious hepatitis and tumors[1]. In the previous researches of chemical constituents, many flavonoids and lignans were isolated from the plants of genus selaginella[2]. In this paper, we report the isolation of two new chromone glycosides, whose structures were determined by 1D and 2D NMR methods, FAB-MS, single-crystal X-ray diffraction techniques and acid hydrolysis.

Figure 1 Structures of **1**~**3**



1 R_1=H R_2=Glc

2 R_1=Ac R_2=Glc

3 R_1=H R_2=H

Compound **1**, yellow powder, obtained from the EtOH extract of this plant, mp. 263-264°C; positive result of molish reaction; UV λ max (MeOH) nm. 217, 263, 300;IR (KBr) 3477(OH), 2931(CH), 1669(C=O) and 1610(C=C) cm^{-1} indicated the presence of OH, C=O and C=C functionalities. Compound **1** exhibited a $[M+H]^+$ ion peak at *m/z*

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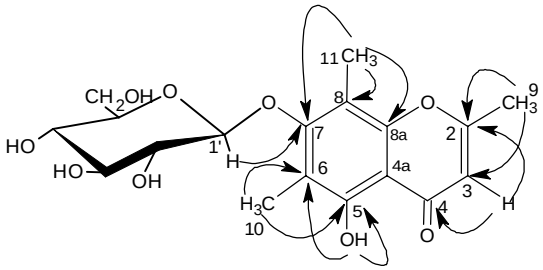
383 in positive FAB-MS corresponding to a molecular formula of $C_{18}H_{22}O_9$. Complete acid hydrolysis of **1** afforded glucose, identified by comparison with authentic samples by TLC. The FAB-MS data 383 $[M+H]^+$ and 221$[M\text{-}Glc+H]^+$ confirmed the above conclusion. The ^1H and ^{13}C NMR spectra (**Table 1**) of **1** clearly showed the presence of chromone skeleton, and there were three methyl and one hydroxy substitutions on the aglycon, which was identified by comparison of its NMR and IR data with those reported in the literatures [3-6]. The sugar residue was clearly indicated by an anomeric carbon signal at δ 104.4, and the corresponding anomeric proton signal at δ 4.63 (d, J=7 Hz). The above data indicated that the glycoside part was β-glucose, and the absolute configuration of β-glucose was assumed to be D.

Figure 2 Key HMBC correlation of **1**



The connectivity of the methyl, hydroxy and glucose at the chromone skeleton of **1** was determined by an analysis of the HMBC, in which correlation peaks were observed between H-1' (δ 4.63) of glucose and C-7 (δ 158.8) of the aglycon, also between H-11 of 8-Methyl (δ 2.29) and C-8 (δ 109.8), C-8a (δ 152.6), C-7 (δ 158.8). The correlation peaks between H-10 (δ 2.17) of 6-Methyl and C-6 (δ 114.3), C-5 (δ 155.9) were also observed. It was concluded that the glucose was bonded to the hydroxyl at C-7 of aglycon, and at the positions of C-6 and C-8 were two methyl substitutions. More over, the HMBC spectrum revealed the correlation peaks between H-9 (δ 2.42) of C-2 Methyl and C-2 (δ 168.4), C-3 (δ 108.0), which confirmed the substitution of Methyl at C-2 position. The correlation peaks were observed between H-3 (δ 6.28) and C-4 (δ 182.7), C-2 (δ 168.4) and C-9 (δ 20.1). The correlation peaks between 5-OH (δ 12.9) and C-5 (δ155.9), C-6 (δ 114.3) and C4a (δ106.5) were also observed (**Figure 1**). Hence, **1** was established to be 5-hydroxy-2, 6, 8-trimethylchromone-7-O-β-D-glucopyranoside, named uncinoside A.

Compound **2**, white powder, also obtained from the EtOH extract of this plant, mp. 165-167°C; positive result of molish reaction; UV λ max (MeOH) nm. 215, 260, 302; IR (KBr) 3365(OH), 2916(CH), 1747(C=O), 1657(OC=O) and 1620(C=C) cm^{-1} indicated the presence of OH, C=O, OC=O and C=C functionalities. Compound **2** exhibited a $[M+H]^+$ ion peak at *m/z* 425 in positive FAB-MS corresponding to a molecular formula of $C_{20}H_{24}O_{10}$. Completed acid hydrolysis of **2** afforded glucose, identified by comparison with authentic samples by TLC. The ^1H and ^{13}C NMR spectra (**Table 1**) of **2** is very similar to **1**, except that there were two additional carbon signals of an acetyl in **2**. The chemical shifts were δ 172.5, δ 20.4 in ^{13}C NMR and δ 1.85 (3H, s) in ^1H NMR, respectively. The FAB-MS data 425 $[M+H]^+$, 263 $[M\text{-}Glc+H]^+$ and 220

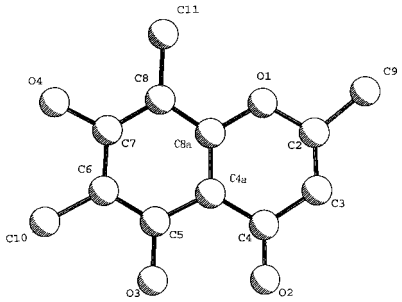
$[M\text{-Glc-Ac}]^+$ confirmed above conclusion. The connectivity of the glucose, methyl and acetyl at the chromone skeleton was determined by HMBC spectra. The acetyl group was connected at 5-OH position of aglycone. This was also confirmed by the absence of 5-OH signal in ^1H NMR spectra, which was clearly observed in **1**. Hence, **2** was established to be 5-acetoxy-2, 6, 8-trimethylchromone-7-O-β-D-glucopyranoside, named uncinoside B.

Table 1 ^1H and ^{13}C NMR data for compound **1** and **2** (δ ppm, 500 MHz in DMSO-d_6)

	Compound **1**		Compound **2**	
No.	δ_C	δ_H	δ_C	δ_H
2	168.4		170.0	
3	108.0	6.28 (1H, s)	109.1	6.09(1H, s)
4	182.7		185.0	
4a	106.5		108.2	
5	155.9	12.94 (1H,s, 5-OH)	157.8	
6	114.3		116.3	
7	158.8		160.2	
8	109.8		111.6	
8a	152.6		154.6	
9	20.1	2.42 (3H, s)	20.5	2.37 (3H, s)
10	9.0	2.17 (3H, s)	8.9	2.17 (3H, s)
11	9.1	2.29 (3H, s)	9.5	2.24 (3H, s)
5-OAc			172.5 (C=O)	
			20.4 (Me)	1.85 (3H, s)
7-O-glc				
1'	104.4	4.63 (1H, d, J=7)	105.7	4.65 (1H, d, J=7.5)
2'	74.1		75.3	
3'	76.3		75.6	
4'	69.9		71.7	
5'	77.0		77.7	
6'	61.0		64.3	

Compound **3** was obtained as yellow crystals, mp. 282-284°C. Its EI-MS gave the $[M]^+$ ion peak at *m/z* 220, corresponding to the molecular formula $C_{12}H_{12}O_4$. Comparing its IR, ^1H and ^{13}C NMR spectra of **3** with these of **1** and analyzing the acid hydrolysis product of **1**, the structure of **3** is elucidated as the aglycone of **1**. The X-ray crystallographic study was performed to confirm the structure of **3**. A view of the solid state conformation is provided in **Figure 3**. The bond lengths were in accordance with expectation′s. Combining with its NMR and MS data, compound **3** was determined as 5,7-dihydroxy-2, 6, 8-trimethylchromone (8-methyl eugenitol). The crystal structure is shown in **Figure 3**.

Figure 3 Stereoview of **3** from X-ray diffraction analysis



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Received 29 October, 2001