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Oldhamioside, A New Phenolic Glucoside from *Daphniphyllum oldhamii*

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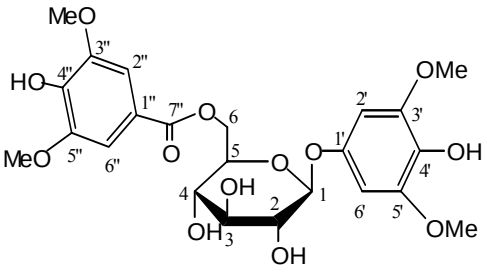
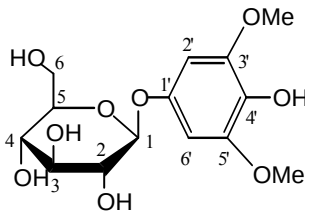
Abstract: Further phytochemical investigation of the ethyl acetate extract of the stem of *Daphniphyllum oldhamii* afforded a new phenolic glucoside, named oldhamioside **1**, together with eleven known compounds, koaburaside **2**, betulin, 28-hydroxyl-3-lupenone, pineresinol, syringaresinol, 4-O-methyl- cedrusin, narigenin, eriodictyol, apigenin, loureirin C, and asperuloside. The structures of new and known compounds were characterized by detailed spectroscopic analysis and comparison of their spectral data with reported values.

Keywords: *Daphniphyllum oldhamii*, phenolic glucoside, oldhamioside, koaburaside.

In the previous papers[1,2], we reported the isolation and structural determination of two new triterpenoids and a new flavan-3-ol glucoside from the stem of *Daphniphyllum oldhamii* (Hemsl.) Rosenth. Recently, on our continuing study on this plant for medicinal agents, a new phenolic compound, named oldhamioside **1**, together with eleven known compounds **2-12**, were isolated from the EtOAc extract of the title plant. The present paper describes the isolation and structural elucidation of the new phenolic glucoside.



1



2

The usual work-up[1] of the EtOAc soluble fraction of methanolic extract of the stem of *D. oldhamii* yielded the new compound **1** and other known compounds.

Compound **1** was obtained as light-yellow fine crystals from MeOH, mp 198-200

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°C, $[\alpha]_D$ - 26.5 (*c* 0.34, MeOH). The positive-ion ESIMS showed a sodiated molecular ion peak at *m*/*z* 535 $[M+Na]^+$. The molecular formula of **1** was determined by HRESIMS as $C_{23}H_{28}O_{13}$ (*m*/*z* $[M+Na]^+$ 535.1412, calcd 535.1428). The IR absorption bands of **1** showed the presence of hydroxyl (3390 cm^{-1}), carbonyl (1699 cm^{-1}), and phenyl (1610, 1508 cm^{-1}) groups. The positive reaction with ferric chloride reagent indicated its phenolic nature. The ^1H NMR spectrum of **1** (**Table 1**) displayed aromatic signals at δ_H 7.16 (s, 2H) and 6.26 (s, 2H), which demonstrated two 1, 3, 4, 5- tetra-substituted aromatic rings. The ^1H NMR spectrum of **1** also exhibited two singlets due to four methoxyl groups at δ_H 3.54 (s, 6H) and δ_H 3.73 (s, 6H), respectively. The above information, together with the observation of an ester carbonyl signal at δ_C 165.6 indicated the presence of a 3-O-5-O-dimethyl-galloyl and 1, 4-dihydroxy- 3, 5- di-methoxy-phenyl units in the molecule. Furthermore, seven sugar protons [δ_H 3.22 (t, 2H, *J* = 7.7 Hz, H-2, H-4), 3.31 (t, 1H, *J* = 7.7 Hz, H-3), 3.75 (m, 1H, H-5), 4.24 (dd, 1H, *J* = 11.3, 6.9 Hz, H-6a), 4.62 (br d, 1H, *J* = 11.3 Hz, H-6b), 4.84 (d, 1H, *J* = 7.7 Hz, H-1)] were observed in the ^1H NMR spectrum of **1**. Using ^1H-^1H COSY and HMQC NMR experiments, these seven sugar protons could be assigned. In addition, the anomeric carbon signal at δ_C 101.0; the methine signals at δ_C 73.2, 76.2, 70.2 and 73.8;

Table 1 ^1H NMR data of compound **1** and ^{13}C NMR data of compounds **1, 2**

	1[a]		**2**[b]
No	δ_H (*J* in Hz)	δ_C	δ_C
1′	-	149.9 (s)	150.3 (s)
2′, 6′	6.26 (s)	95.0 (d)	95.2 (d)
3′, 5′	-	148.1 (s)	148.1 (s)
4′	-	130.5 (s)	130.5 (s)
3′, 5′ -OCH_3,	3.54 (s)	55.7 (q)	55.9 (q)
1	4.84 (d, 7.7)	101.0 (d)	101.8 (d)
2	3.22 (t, 7.7)	73.2 (d)	73.4 (d)
3	3.31 (t, 7.7)	76.2 (d)	77.2 (d)
4	3.22 (t, 7.7)	70.2 (d)	70.2 (d)
5	3.75 (m)	73.8 (d)	76.8 (d)
6a	4.62 (br d, 11.3)	64.2 (t)	61.0 (t)
6b	4.24 (d, 11.5, 6.9)		
1″	-	119.4 (s)	
2″, 6″	7.16 (s)	106.9 (d)	
3″, 5″	-	147.5 (s)	
4″	-	140.8 (s)	
3″, 5″ -OCH_3,	3.73 (s)	56.0 (q)	
7″	-	165.6 (s)	

[a] Bruker AMX 400 MHz; Measured in DMSO-d_6. Chemical shifts ( ) are expressed relative to TMS. Assignments were deduced by analysis of 1D and 2D spectra.
[b] Measured in DMSO-d_6.[3]

and the methylene signal at δ_C 64.2 in the ^{13}C NMR spectrum indicated that the monosaccharide unit was glucose, which was also established by comparison on TLC with the standard sugar after hydrolysis. The configuration of the anomeric proton of the glucose was proposed as β on the basis of the coupling constant (J = 7.7 Hz) of the ^1H NMR signal at δ 4.84. The respective positions of the substituents were determined using long-range heteronuclear correlations observed by HMBC. The correlations showed three-bond coupling from H-1 to C-1' and H-6 to C-7" which indicated that the C-1' and carboxylic C-7" were attached to the glucose C-1 and C-6, respectively. In fact, the spectral data of **1**, except for the 3-O-5-O-dimethyl-galloyl unit, were very similar to these of the co-occurring known compound **2** (**Table 1**). The structure for oldhamioside, therefore, was assigned as **1**.

The structures of known compounds were determined as koaburaside **2**[3], betulin **3**[4], 28-hydroxyl-3-lupenone **4**[4], pineresinol **5**[5], syringaresinol **6**[6], 4-O-methyl-cedrusin **7**[7], narigenin **8**[8], eriodictyol **9**[8], apigenin **10**[8], loureirin C **11**[9], and asperuloside **12**[10], respectively, by detailed spectroscopic analysis and comparison of their spectral data with reported values in the literatures.

Compound **1** has not been isolated previously from natural source while the known compounds **2-12** were obtained from *D. oldhamii* for the first time. The immune and antitumor activities of compounds **1**, **2** were tested, both of them showed no significant bioactivity. Other bioassays for these compounds are currently ongoing.

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