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A new benzophenone *C*-glycoside from *Polygala telephioides* Willd.

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Abstract

A new benzophenone *C*-glucoside, 3′-*C*-[4-*O*-(5-hydroxyferuloyl)-β-D-glucopyranosyl]-2′,4′,6′-trihydroxy-3,4-dimethoxybenzophenone, named telephenone D, was isolated from the whole plants of *Polygala telephioides*, and its structure was determined by analysis of spectroscopic data.

Keywords: *Polygala telephioides*; Benzophenone *C*-glucoside; Telephenone D

Polygala telephioides Willd. is widely distributed in southern China and has been used as a detoxification agent for heroin poisoning in China. It was reported to contain oligosaccharide esters, benzophenone *C*-glucosides and the flavone *C*-glucoside, telephioidin in the above mentioned plant [1–3]. Here, we report the isolation and structure elucidation of a new benzophenone *C*-glucoside, telephenone D (**1**), from the whole plants of *P. telephioides*. Naturally occurring benzophenone *C*-glucosides are very rare, and to our knowledge, only five compounds with this skeleton have been reported from the plants of the genus *Polygala* [1,2,4,5].

The dried whole plants (18 kg) of *P. telephioides* were extracted twice with hot 95% ethanol for 2 h each time under reflux. After removal of the solvent under reduced pressure at 60 °C, the residue (1.15 kg) was suspended in water and defatted with petroleum ether. The aqueous layer was further extracted with ethyl acetate and *n*-butanol successively to obtain the EtOAc extract (120 g) and *n*-butanol extract (680 g). A portion of *n*-butanol extract (600 g) was subjected to D101 porous polymer resin and eluted with H_2O, 20%, 50% and 70% aqueous EtOH successively. The 50% aqueous EtOH eluate (140 g) was chromatographed on a silica gel (200–300 mesh, 1 kg) column using $CHCl_3$–MeOH in a gradient manner (10:1 → 1:1) to afford nine fractions (A–I) on the basis of TLC analyses. Subfraction D (12.0 g) was applied to a silica gel (200–300 mesh, 100 g) column, eluted with $CHCl_3$–MeOH–H_2O (20:1:0.1 → 3:1:0.1) to give six fractions based on TLC. Among them, Fr. 5 (20.3 g) was first subjected to silica gel CC using $CHCl_3$/MeOH (20:1 → 1:1) as eluent, then purified by Sephadex LH-20 column chromatography to yield compound **1** (18 mg).

Compound **1** was obtained as a pale yellow powder, and its positive-ion ESI-TOF-MS exhibited quasi-molecular ion peaks $[M+H]^+$, $[M+Na]^+$ and $[M+K]^+$ at *m/z* 645.1, 667.0 and 683.0, respectively, indicating the molecular formula to be $C_{31}H_{32}O_{15}$. HRESIMS: *m/z* 645.1609$[M+H]^+$ (Cacld. for $C_{31}H_{33}O_{15}$, 645.1602). IR spectrum showed

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Table 1
^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) data for compound **1** (in DMSO-d_6).

Position	δ_C	δ_H	Position	δ_C	δ_H
1	132.4		3-OMe	55.9	3.77 *s*
2	111.1	7.26 *d* (2.1)	4-OMe	55.6	3.81 *s*
3	152.2				
4	148.0		5-Hydroxyferuloyl		
5	110.4	6.98 *d* (8.1)	1‴	124.4	
6	123.8	7.22 *dd* (2.1, 8.1)	2‴	103.4	
1′	106.0		3‴	148.5	
2′	158.9		4‴	137.1	
3′	103.6		5‴	144.9	
4′	160.4		6‴	110.2	
5′	94.9	5.98 *s*	3‴-OMe	55.4	3.79 *s*
6′	157.7		α	114.6	6.39 *d* (15.9)
C═O	195.4		β	145.6	7.46 *d* (15.9)
Glc-1″	74.4	4.62 *d* (6.0)	C═O	165.9	
2″	71.4	3.90 *m*			
3″	76.0	3.47(overlapped)			
4″	71.2	4.80 *t* (8.0)			
5″	79.0	3.46(overlapped)			
6″	60.7	3.32 *m*, 3.48 *m*			

absorptions due to hydroxyl (3305 cm^{-1}), carbonyl (1655 cm^{-1}), aromatic ring (1633, 1604, 1513, 1452 cm^{-1}). UV (MeOH) λ_{max} (log ε): 315 (3.04), 213 (2.54) nm; UV(MeOH + NaOAC) λ_{max} (log ε): 375, 230 nm; acid hydrolysis of compound followed by GC analysis showed the presence of a glucose. We favor its D absolute configuration by comparison of its retention time (t_R = 12.50 min) with that of authentic standard. The ^{1}H NMR spectrum showed an isolated aromatic proton at δ 5.98 (s, 1H), ABX-system aromatic protons at δ 7.26 (d, 1H, J = 2.1 Hz), 7.22 (dd, 1H, J = 2.1, 8.1 Hz) and 6.98 (d, 1H, J = 8.1 Hz), a pair of *E*-olefinic protons at δ 7.46 (d, 1H, J = 15.9 Hz) and 6.39 (d, 1H, J = 15.9 Hz), two *meta*-aromatic protons at δ 6.90 (d, 1H, J = 1.5 Hz) and 6.71 (d, 1H, J = 1.5 Hz), three methoxyl protons at δ 3.77 (s, 3H), 3.79 (s, 3H) and 3.81 (s, 3H), and a sugar unit with the anomeric H-atom resonated at δ 4.62 (d, 1H, J = 6.0 Hz). The ^{13}C NMR (Table 1) spectrum exhibited 31 signals in total, among which were presence of a 5-hydroxyferuloyl in **1**. All the H- and C-atoms were assigned by ^{1}H, ^{1}H-COSY, NOESY, HSQC and HMBC

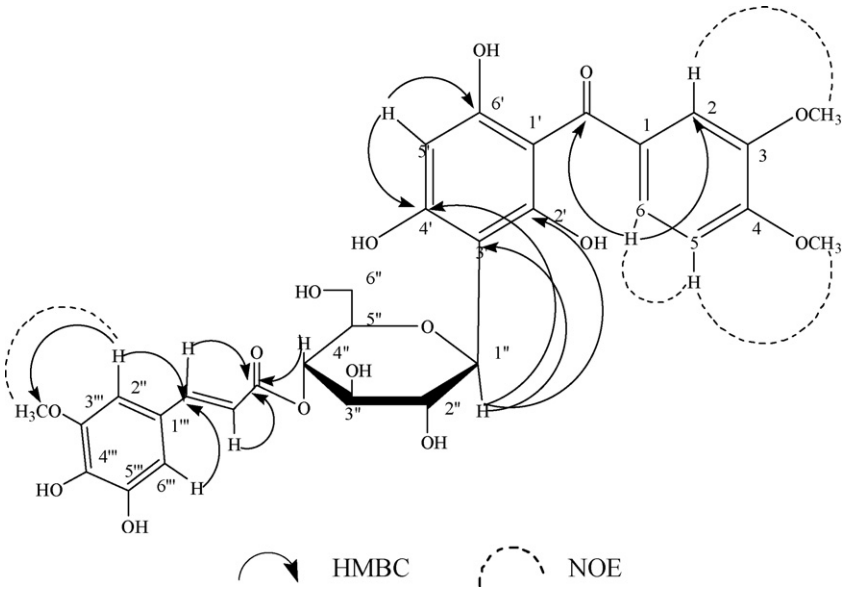

Fig. 1. Key NOE and HMBC correlations of compound **1**.

experiments, we deduced that the C-4 position of the Glc in **1** was esterified by a 5-hydroxyferulic acid. The HMBC spectrum, as shown in Fig. 1, revealed that the 5-hydroxyferuloy residue was attached to the C-4 of the glucosyl moiety, which showed a cross-peak between the proton signal at δ 4.80 (H-4 of Glc) and the carbonyl carbon signal at δ 165.9. From the above data, the structure of **1** was established to be 3′-*C*-[4-*O*-(5-hydroxyferuloyl)-β-D-glucopyranosyl]-2′,4′,6′-trihydroxy-3, 4-dimethoxy benzophenone, named telephenone D.

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