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Hepatoprotective acyl glycosides obtained from *Erycibe hainanesis*

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ABSTRACT

An ongoing search for naturally occurring hepatoprotective constituents has identified three new acyl glycosides (**1**–**3**) and a new lignan glycoside (**4**) in the roots and stems of *Erycibe hainanesis* using various column chromatography methods. The structures of these compounds have been determined based on chemical and spectroscopic evidence, and the following bioassay indicates that all four glycosides have moderate hepatoprotective activities against D-galactosamine induced toxicity in WB-F344 rat hepatic epithelial stem-like cells.

1. Introduction

Acyl glycosides are known to display hepatoprotective activities (Wei et al., 2013; Tian et al., 2013; Song et al., 2010; Feng et al., 2013). Our previous studies of the constituents of *Erycibe hainanesis*, a climbing shrub belonging to family Convolvulaceae, indicated that this plant contains glycosides of coumarins, phenolic, and terpenes (Song et al., 2010; Feng et al., 2013). Most of these glycosides possess syringoyl (or vanilloyl)-glycosyl moieties and demonstrate hepatoprotective activities against D-galactosamine-induced toxicity. The present study was taken up to isolated the secondary metabolites from *E. hainanesis* and evaluated them for hepatoprotective activity. Three new acyl glycosides (**1**–**3**) and a new lignan glycoside (**4**) were obtained (Fig. 1). Their structures have been determined by UV, IR, 1D and 2D NMR spectroscopy and HRESIMS data along with chemical methods. Two known acyl glycosides, khaephuoside B (**5**) (Kanchanapoom et al., 2002) and albibrissinoside A (**6**) (Jung et al., 2004), and the known chlorogenic acid derivative butyl 3,4-dicaffeoylquinate (**7**) (Um et al., 2002) have also been identified. In subsequent *in vitro* assays, compounds **1**–**4** demonstrated moderate hepatoprotective activities against D-galactosamine induced cytotoxicity in WB-F344 rat hepatic epithelial stem-like cells.

2. Results and discussion

Compound **1** was obtained as a white powder, $[\alpha]_D^{20}$ − 66.4 (*c* 0.13, MeOH). The positive HRESIMS data of **1** indicated an $[M + Na]^+$ ion at *m/z* 585.2147, corresponding to the molecular formula $C_{25}H_{38}O_{14}$ (calculated for $C_{25}H_{38}O_{14}Na$, 585.2154). The ^1H NMR spectrum contains the characteristic proton signals of a syringoyl moiety at δ_H 7.24 (2H, s) and 3.80 (6H, s) and other signals corresponding to an oxymethylene at δ_H 3.72 (1H, m, H-1a) and 3.26 (1H, m, H-1b), a methylene at δ_H 1.29 (2H, m, H-2), a methine at δ_H 1.50 (1H, m, H-3), and two methyls at δ_H 0.71 (3H, d, J = 6.5 Hz, H-4) and 0.70 (3H, d, J = 6.0 Hz, H-5), the combination of which implies that an isoamyl alcohol moiety existed in **1**. Furthermore, two doublets due to anomeric protons at δ_H 4.13 (1H, d, J = 7.5 Hz, H-1′) and 5.34 (1H, br s, H-1″) together with the partially overlapped signals between δ 3.04 and 4.30 indicated the presence of two sugar moieties. The ^{13}C NMR spectrum (Table 1) showed 25 carbon signals; of these, one carbonyl carbon signal at δ_c 165.5, two methoxyl carbons, and six aromatic carbons corresponded to the syringoyl moiety, and five carbon signals corresponded to the isoamyl alcohol moiety. The remaining 11 signals indicated the existence of one hexose and one pentose. Subsequently, their D-configurations were determined by NMR data comparison (Kim et al., 2010) and gas chromatographic analysis of derivatization (Hara et al., 1987). Furthermore, anomeric chemical shifts and coupling constants (glc: J = 7.5 Hz; api: J = br s) confirmed β-configurations (Smite et al., 1993). The linkage positions were

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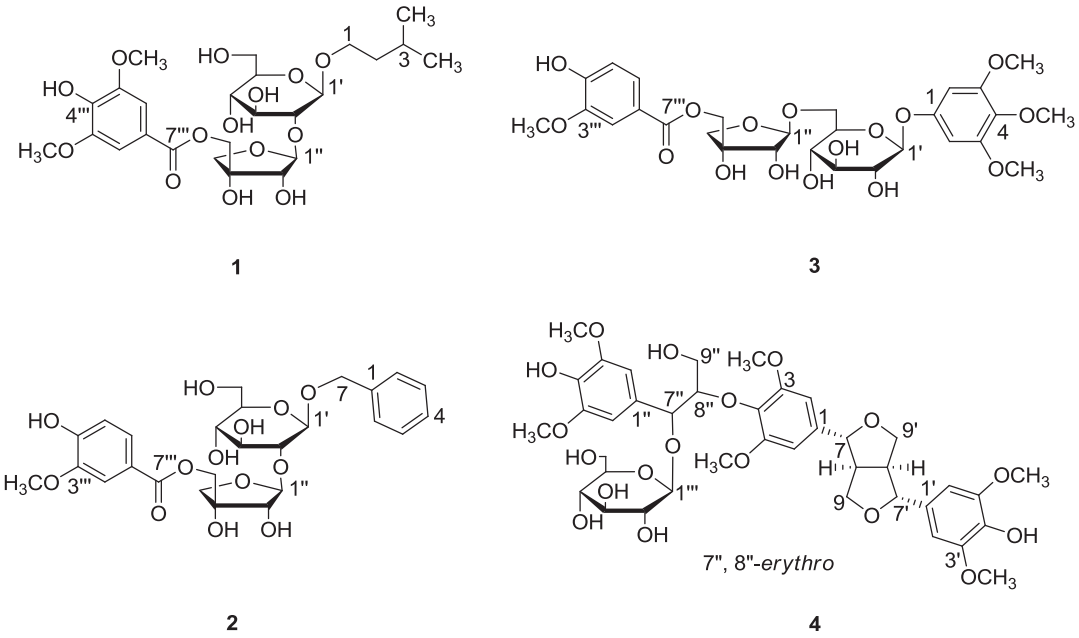

Fig. 1. Structures of compounds **1**–**4**.

established as β-D-apiofuranosyl-(1 → 2)-β-D-glucopyranosyl based on the HMBC correlations from H-1″ to C-2′ (δ_c 77.3) (Fig. 2). Moreover, in the HMBC experiment, the correlation between H-5″ and C-7‴ suggested the formation of an esterifiable position at C-api-5. Thus, the sugar chain was determined to be 2-*O*-(5-*O*-syringoyl-β-D-apiofuranosyl)-β-D-glucopyranosyl. The HMBC spectrum showed correlations of C-1 with H-1′, C-1′ with H-1, C-1″ with H-2′, and C-7‴ with H-5″, and therefore the compound **1** was determined as 1-*O*-[2-*O*-(5-*O*-syringoyl-β-D-apiofuranosyl)-β-D-glucopyranosyl]-isoamyl alcohol.

Table 1
^{1}H and ^{13}C NMR spectroscopic data of compounds **1**–**3**.[a]

Position	1		2		3	
	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	δ_C
1	3.72 m	66.9		137.7		153.9
	3.26 m					
2	1.29 m	37.9	7.29 d (7.0)	127.6	6.32 s	94.3
3	1.50 m	24.4	7.22 t (7.0)	128.0		153.1
4	0.71 d (6.5)	22.4	7.22 t (7.0)	127.3		132.5
5	0.70 d (6.0)	22.3	7.22 t (7.0)	128.0		153.1
6			7.29 d (7.0)	127.6	6.32 s	94.3
7			4.77 d (12.0)	69.6		
			4.47 d (12.0)			
1′	4.13 d (7.5)	101.1	4.30 d (7.0)	100.3	4.78 d (7.5)	100.8
2′	3.21 m	77.3	3.27 m	76.6	3.19 m	73.1
3′	3.04 m	76.6	3.09 m	76.4	3.06 m	76.9
4′	3.23 m	70.3	3.09 m	70.3	3.26 m	70.0
5′	3.04 m	76.7	3.68 m	76.8	3.51 m	75.4
6′	3.64 m	60.9	3.70 m	61.0	3.77 m	67.6
	3.41 m		3.44 m		3.41 dd (11.0, 8.0)	
1″	5.34 br s	108.1	5.33 br s	108.4	4.87 d (3.0)	108.7
2″	3.80 overlapped	75.6	3.82 br s	77.1	3.65 overlapped	77.0
3″		77.5		77.4		76.4
4″	4.03 d (9.0)	73.8	3.89 d (9.0)	73.8	3.93 d (9.5)	73.3
	3.72 d (9.0)		3.62 d (9.0)		3.91 d (9.5)	
5″	4.30 d (11.0)	67.8	4.24 d (11.5)	67.2	4.19 br s	66.2
	4.19 d (11.0)		4.14 d (11.5)			
1‴		119.2		120.3		120.5
2‴	7.24 s	107.3	7.43 br s	112.8	7.44 br s	112.8
3‴		147.5		147.3		147.4
4‴		140.9		150.8		151.0
5‴		147.5	6.85 d (8.0)	115.1	6.86 d (8.0)	115.2
6‴	7.24 s	107.3	7.47 d (8.0)	123.7	7.49 d (8.0)	123.6
7‴		165.5		165.4		165.4
3/5-OMe					3.70 s	55.7
4-OMe					3.56 s	60.0
3‴-OMe	3.80 s	56.1	3.82 s	55.7	3.80 s	55.6
5‴-OMe	3.80 s	56.1				

[a] NMR data (δ) were measured in DMSO-d_6 at 500 MHz for ^{1}H NMR, and at 125 MHz for ^{13}C NMR. Coupling constants (*J*) in Hz are given in parentheses.