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Hydroquinone diglycoside acyl esters from the stems of *Glycosmis pentaphylla*

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Abstract

Four hydroquinone diglycoside acyl esters, glypentosides A–C (**1**–**3**) and seguinoside F (**4**), were isolated from the stems of *Glycosmis pentaphylla*. Glypentosides A–B (**1**–**2**) were identified as compounds and designated as methoxyquinol 4-*O*-[(5-*O*-*trans*-*p*-coumaroyl)-β-D-apiofuranosyl-(1 → 2)-β-D-glucopyranoside] (**1**) and 4-demethylantiarol 4-*O*-[(3-methoxy-4-hydroxy-benzoyl)-β-D-apiofuranosyl-(1 → 2)-β-D-glucopyranoside] (**2**). Glypentoside C (**3**) is a hydroquinone diglycoside acyl ester with a neolignan moiety in the acyl unit. Their structures were elucidated by the combination of one- and two-dimensional NMR analysis, mass spectrometry and chemical evidences.

Keywords: *Glycosmis pentaphylla*; Rutaceae; Glypentosides A–C; Hydroquinone glycosides; Acyl esters; Apiosyl-(1 → 2)-glucosides

1. Introduction

The genus *Glycosmis* of the family Rutaceae is represented in China by nearly 11 species (Huang, 1997). *Glycosmis pentaphylla* (Retz.) DC. is a shrub or small (1.5–5 m) tree widely distributed from India, Malaysia and southern China to the Philippine Islands where it occurs in tropical forests at low altitudes. It has been used as a folk medicine in the treatment of fever, liver complaints and certain other diseases (Sastri, 1956). Phytochemical researches of this species were mainly focused on hydrophobic alkaloids, including those of the quinolone (Bhattacharyya and Chowdhury, 1985), quinazoline (Muthukrishnan et al., 1999; Sarkar and Chakraborty, 1979), acridone (Quader et al., 1999) and carbazole (Jash et al., 1992; Chowdhury et al., 1987) types, of leaves, root and stem bark. No study on glycosidic constituents of *G. pentaphylla* has been reported. In this paper, we present results of an study on the polar constituents of the stem wood of the plant.

2. Results and discussion

The EtOAc-soluble fraction of the MeOH extract was subjected to a succession of chromatographic procedures and finally by preparative ODS-HPLC to give three new hydroquinone diglycosides, namely glypentoside A (**1**), glypentoside B (**2**) and glypentoside C (**3**), besides the known compound seguinoside F (**4**). The known compound was identified by comparing its spectral data with those previously reported (Zhong et al., 1998).

Compound **1** was isolated as amorphous powder. Its molecular formula $C_{27}H_{32}O_{14}$ was deduced from the negative HRFABMS spectrum and ^{13}C NMR spectral data. The IR spectrum showed absorption bands due to hydroxyl (3420 cm^{-1}) and carbonyl groups (1690 cm^{-1}). The ^{1}H NMR signals due to aromatic and olefinic protons at δ 7.54 (1H, *d*, $J = 15.7$ Hz), 7.37 (2H, *d*, $J = 8.4$ Hz), 6.79

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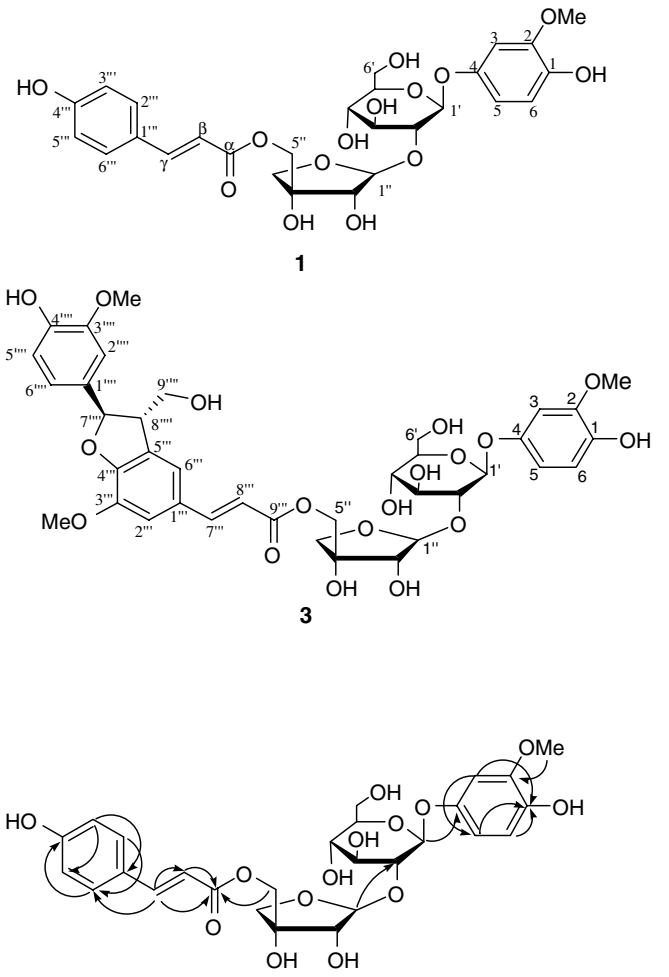

Fig. 1. Selected HMBC correlations of **1**.

Table 1
The ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) data of **1** and **2** in CD_3OD (*J* in Hz within parentheses)

No.	**1**		**2**	
	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	δ_C
1		142.9 *s*		155.5 *s*
2		149.2 *s*	5.99 *s*	94.5 *d*
3	6.70 *d* (2.4)	103.4 *d*		154.8 *s*
4		152.6 *s*		128.5 *s*
5	6.48 *dd* (2.4, 8.2)	109.6 *d*		154.8 *s*
6	6.62 *d* (8.2)	116.1 *d*	5.99 *s*	94.5 *d*
1′	4.80 *d* (7.3)	102.0 *d*	4.94 *d* (7.6)	102.7 *d*
2′	3.58–3.65	78.8 *d*	3.62–3.72	78.8 *d*
3′	3.58–3.65	78.5 *d*	3.62–3.72	78.5 *d*
4′	3.33–3.36	71.7 *d*	3.33–3.37	71.7 *d*
5′	3.33–3.36	78.1 *d*	3.33–3.37	78.1 *d*
6′	3.58–3.65, 3.85[a]	62.6 t	3.62–3.72, 3.82[a]	62.6 *t*
1″	5.48 *d* (1.8)	110.5 *d*	5.50 *d* (2.2)	110.5 *d*
2″	4.02 *d* (1.8)	78.7 *d*	4.00 *d* (2.2)	78.7 *d*
3″		79.2 *s*		79.6 *s*
4″	Ha 3.88 *d* (9.5)	75.4 *t*	Ha 3.90 *d* (9.8)	75.7 *t*
	Hb 4.28 *d* (9.5)		Hb 4.38 *d* (9.8)	
5″	Ha 4.26 *d* (11.2)	67.6 *t*	Ha 4.36 *d* (10.8)	67.8 *t*
	Hb 4.37 *d* (11.2)		Hb 4.43 *d* (10.8)	
1‴		127.1 *s*		122.4 *s*
2‴	7.37 *d* (8.4)	131.2 *d*	7.44 *d* (1.8)	113.6 *d*
3‴	6.79 *d* (8.4)	116.9 *d*		152.9 *s*
4‴		161.3 *s*		148.6 *s*
5‴	6.79 *d* (8.4)	116.9 *d*	6.78 *d* (8.2)	115.9 *d*
6‴	7.37 *d* (8.4)	131.2 *d*	7.47 *dd* (8.2,1.8)	125.2 *d*
α		168.8 *s*		168.1 *s*
β	6.20 *d* (15.7)	114.8 *d*		
γ	7.54 *d* (15.7)	146.9 *d*		
OMe	3.86 *s*	56.4 *q*	3.83 *s* (MeO-3‴)	56.3 *q* (MeO-3‴)
			3.70 *s* (MeO-3,5)	56.7 *q* (MeO-3,5)

[a] Signal pattern unclear due to overlapping.

(2H, *d*, *J* = 8.4 Hz), 6.20 (1H, *d*, *J* = 15.7 Hz), as well as one ester carbonyl carbon at *δ* 168.8, suggested the presence of one *trans-p*-coumaroyl moiety. The ^{1}H and ^{13}C NMR spectra of **1** (Table 1) also revealed the presence of glucopyranose and apiofuranose moieties. The β-anomeric configuration for the glucopyranose was determined from a large coupling constant value (7.3 Hz) of the anomeric proton (Agrawal, 1992; Ishii and Yanagisawa, 1998). The β-anomeric configuration for the apiofuranose was indicated from the anomeric signals at δ_C 110.5 (Kitagawa et al., 1993) with δ_H 5.48 (1H, *d*, *J* = 1.8 Hz) (Mbaïraroua et al., 1994; Otsuka et al., 1994). On acid hydrolysis, **1** afforded D-glucose and D-apiose as component sugars, which was identified by TLC and GLC analysis. The apiosyl-(1 → 2)-glucosyl linkage of the glycosidic moiety was assigned from the cross-peaks observed between apiose H-1 and glucose H-2 in the NOESY spectrum. Also in the HMBC spectrum (Fig. 1) of **1**, a correlation was evident between apiose H-1 (*δ* 5.48) and glucose C-2 (*δ* 78.8). The position was confirmed by the chemical shift (*δ* 78.8) of glucose C-2, as compared with a nonsubstituted C-2, which is ca. *δ* 74.0. All chemical shifts of this sugar moiety are in good agreement with the literature data (Zhong et al., 1998). The significant deshielding of H-5 of apiose (4.26 and 4.37 ppm) and the HMBC cross-peak between the proton at 4.37 ppm and the carbonyl carbon at 168.8 ppm confirmed that the coumaroyl unit was attached to position 5 of apiose.

The ^{13}C NMR spectrum of **1** showed, for the aglycon portion, seven signals. These were assigned to a methoxy group, three to aromatic CH, and three to phenolic functions. The ^{1}H NMR spectrum contained the signals for three aromatic protons at *δ* 6.70 (1H, *d*, *J* = 2.4 Hz), 6.62 (1H, *d*, *J* = 8.2 Hz), and 6.48 (1H, *dd*, *J* = 2.4, 8.2 Hz), along with a signal for a methoxy group at *δ* 3.86, which correlated in the HMBC spectrum with a signal at δ_C 149.2, corresponding to a typical methoxyquinol. The site of glycosidation was revealed to be C-4 by HMBC experiment, which showed a long-range correlation between C-4 (*δ* 152.6) and the anomeric proton (*δ* 4.80) of glucose, which was further supported by the NOE cross-peaks (Fig. 2) observed from the anomeric proton (*δ* 4.80) of glucose to two aromatic protons at δ_H 6.48 (1H, *dd*, *J* = 2.4, 8.2 Hz) and 6.70 (1H, *d*, *J* = 2.4 Hz). Based on the above results, the structure of glycopentoside A (**1**) was established as methoxyquinol 4-*O*-(5-*O*-*trans-p*-coumaroyl)-β-D-apiofuranosyl-(1 → 2)-β-D-glucopyranoside.