Phytochemistry Letters 5 (2012) 240–243

Contents lists available at ScienceDirect

Phytochemistry Letters

journal homepage: www.elsevier.com/locate/phytol

Two new neolignan glycosides from *Pittosporum glabratum* Lindl.

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ARTICLE INFO

Article history:
Received 15 November 2011
Received in revised form 19 December 2011
Accepted 5 January 2012
Available online 19 January 2012

Keywords:
Pittosporum glabratum Lindl.
Chemical constituents
Neolignan glycosides

ABSTRACT

Two new neolignan glycosides, named pittogoside A (**1**) and pittogoside B (**2**) were isolated from the roots of *Pittosporum glabratum* Lindl. Their structures, including the absolute stereochemistry, were determined on the basis of spectroscopic analysis and chemical evidence, with combination of circular dichroism.

1. Introduction

The roots of *Pittosporum glabratum* Lindl. (Pittosporaceae), commonly called "Shan Zhi Gen" in Chinese, have been known for its analgesic and antidotal activities in the folk medicine (Anon., 1993). As part of our current interest in biologically active compounds of folk medicine in China, we investigated the chemical constituents of the roots of *P. glabratum* and reported the isolation of two iridoid glycosides and five lignan glycosides from its EtOH extract (Nie et al., 2011). Our continuing phytochemical studies on this extract led to the isolation of two new benzofuran-type neolignan glycosides, pittogosides A (**1**) and B (**2**). In this paper, we reported the isolation and structural elucidation of two new neolignan glycosides (Fig. 1).

2. Results and discussion

Pittogoside A (**1**) was obtained as a white amorphous powder. The molecular formula was determined to be $C_{36}H_{44}O_{16}$ by HRESI-MS (*m/z* 755.2528 $[M+Na]^+$, calcd for 755.2522). The IR spectrum suggested the presence of hydroxyl group (3340 cm^{-1}), carbonyl group (1705 cm^{-1}) and aromatic ring (1599 and 1515 cm^{-1}). Enzymatic hydrolysis of **1** afforded D-glucose, which was identified by HPLC analysis of its 1-[(*S*)-*N*-acetyl-α-methylbenzylamino]-1-deoxyglucitol acetate derivative (Oshima et al., 1982). The β-anomeric configuration for glucose was determined by its large $^3J_{H-1,H-2}$ coupling constant value (6.6 Hz). Analysis of the ^1H NMR spectrum showed the presence of a syringoyl group due to a singlet for two aromatic protons at δ_H 7.59 (2H, s) and a singlet for two methoxyl groups at δ_H 3.71 (6H, s), which was supported by the corresponding carbon signals at δ_C 166.5, 148.4, 142.5, 120.1, 107.9 and 55.9 in the ^{13}C NMR spectrum (Jung et al., 2004; Yang et al., 2006). Except for the signals due to a glucopyranose unit and a syringoyl group, the remaining 21 carbons were assignable to the aglycone. Taking account of the 15 degree of unsaturation calculated from the molecular formula of **1**, it was suggested that the aglycone of **1** should have at least two aromatic rings. The ^1H NMR data of the aglycone moiety showed a set of characteristic signals due to dihydrobenzofuran at δ_H 6.04 (1H, d, J = 6.6 Hz) and δ_H 3.85 (1H, m), a set of signals due to *n*-propanol group at δ_H 3.89 (1H, t, J = 6.6 Hz), 2.83 (1H, t, J = 7.8 Hz) and 2.05 (1H, m), four aromatic proton signals at δ_H 7.03 (2H, s), 7.01 (1H, s) and 6.89 (1H, s), two hydroxymethyl protons at δ_H 4.23 (1H, m) and 4.17 (1H, m), and three methoxy groups at δ_H 3.62 (6H, s) and 3.80 (3H, s) (Table 1). Two partial structures of the aglycone (C-7 to C-9 and C-7′ to C-9′) were deduced from the detailed analyses of the ^1H–^1H COSY spectrum of **1** (Fig. 2). Interpretation of the HMBC spectral data led to the connections of the above-described structural units and quaternary carbons to construct the whole structure of the aglycone. The HMBC correlations from δ_H 6.89 (H-2′) to δ_C 136.1 (C-1′), 144.4 (C-3′), 146.9 (C-4′) and 117.2 (C-6′), δ_H 7.01 (H-6′) to δ_C 146.9 (C-4′), 129.5 (C-5′) and 54.9 (C-8), and δ_H 4.23, 4.17 (H-9) to δ_C 129.5 (C-5′) indicated the connectivity of rings A and B (Fig. 2). The other aromatic ring, namely ring C and its linkage was suggested by the HMBC correlations from δ_H 7.03 (H-2 and H-6) to δ_C 139.0 (C-1), 153.9 (C-3 and C-5), 135.0 (C-4) and 87.7 (C-7). Three methoxy groups were assigned to be located in C-3, C-5 and C-3′ by the correlations between their protons and chemical shift assigned carbons of C-3, C-5 and C-3′. In addition, a hydroxypropyl group was attached at C-1′ on the basis of the correlation from δ_H 2.83 (H-7′) to δ_C 136.1 (C-1′). The relative stereochemistry of H-7

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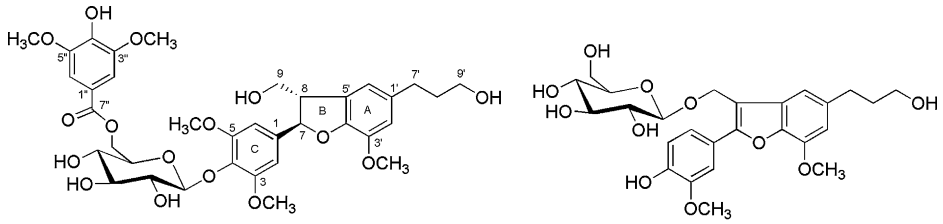
doi:10.1016/j.phytol.2012.01.003



1 **2**

Fig. 1. Structures of compounds **1** and **2**.

Table 1
^{1}H (600 MHz) and ^{13}C NMR (150 MHz) data of **1** in C_5D_5N and **2** in CD_3OD.

Position	1		Position	2	
	δ_H	δ_C		δ_H	δ_C
1		139.0	1		121.8
2	7.03 (s)	104.3	2	7.53 (d, 1.8)	110.5
3		153.9	3		147.8
4		135.0	4		147.5
5		153.9	5	6.95 (d, 8.0)	115.1
6	7.03 (s)	104.3	6	7.45 (dd, 8.0, 1.8)	120.6
7	6.04 (d, 6.6)	87.7	7		155.6
8	3.85 (m)	54.9	8		131.9
9	4.23[a]	64.0	9	5.10 (d, 12.0)	60.3
	4.17[a]			4.97 (d, 12.0)	
1′		136.1	1′		138.0
2′	6.89 (s)	113.3	2′	6.78 (s)	107.3
3′		144.4	3′		144.7
4′		146.9	4′		141.2
5′		129.5	5′		110.0
6′	7.01 (s)	117.2	6′	7.22 (s)	110.8
7′	2.83 (t, 7.8)	32.4	7′	2.80 (t, 7.2)	32.0
8′	2.05 (m)	35.8	8′	1.94 (m)	34.6
9′	3.89 (t, 6.6)	61.2	9′	3.63 (t, 6.6)	60.8
1″		120.1			
2″, 6″	7.59 (s)	107.9			
3″, 5″		148.4			
4″		142.5			
7″		166.5			
3,5-OCH_3	3.62 (s)	56.2	3-OCH_3	3.99 (s)	55.3
3′-OCH_3	3.80 (s)	55.8	3′-OCH_3	4.02 (s)	55.0
3″,5″-OCH_3	3.71 (s)	55.9			
Glc-1	5.71 (d, 6.6)	104.7	Glc-1	4.50 (d, 7.8)	101.3
Glc-2	4.35[a]	75.7	Glc-2	3.33[a]	73.8
Glc-3	4.35[a]	77.9	Glc-3	3.33[a]	76.7
Glc-4	4.23[a]	71.4	Glc-4	3.33[a]	70.3
Glc-5	4.17[a]	75.5	Glc-5	3.33[a]	76.7
Glc-6	5.14 (br.d, 12.0)	64.8	Glc-6	3.95 (dd, 11.7, 1.8)	61.4
	5.00 (dd, 12.0, 6.0)			3.77 (dd, 11.7, 6.0)	

[a] Overlapped.

and H-8 was established as *trans* relationship based on the $^{3}J_{H\text{-}7,H\text{-}8}$ coupling constant (6.6 Hz) (Yuan and Li, 2003; Matsuda et al., 1996). Thus, the structure of the aglycone of **1** was concluded as 5-methoxy-dihydrodehydrodiconiferyl alcohol (**1a**) (Chin et al., 2008), which was obtained by enzymatic hydrolysis. It was worth mentioning that enzymatic hydrolysis of **1** with cellulase gave not only **1a** and D-glucose, but also syringic acid (**1b**) (Xu et al., 2010) and a desyringoyl derivative of **1** (5-methoxy-dihydrodehydrodiconiferyl alcohol-4-*O*-β-D-glucopyranoside, **1c**) (Wang et al., 2010) (Scheme 1), which were identified by the ^{1}H NMR and ESI-MS data. To determine the absolute configuration of the aglycone, circular dichroic method was applied. As a negative cotton effect at 244 nm ($\Delta\varepsilon = -0.61$) was observed, 7*R* and 8*S* configurations were indicated (Matsuda et al., 1996; Iida et al., 2010; Lemiere et al., 1995). The β-D-glucopyranose was linked to C-4 of the aglycone by the HMBC correlation from δ_H 5.71 (Glc-H-1) to δ_C 135.0 (C-4) and the location of syringoyl group at C-6 of β-D-glucopyranose was deduced by the correlation from δ_H 5.14, 5.00 (Glc-H-6) to δ_C 166.5 (C-7″). Based on the above evidences, the structure of **1** was established as (7*R*,8*S*)-5-methoxy-dihydrodehydrodiconiferyl alcohol-4-*O*-(6″-*O*-syringoyl)-β-D-glucopyranoside.

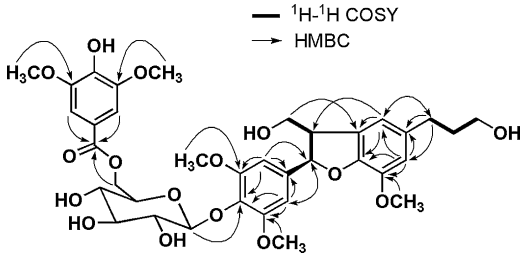
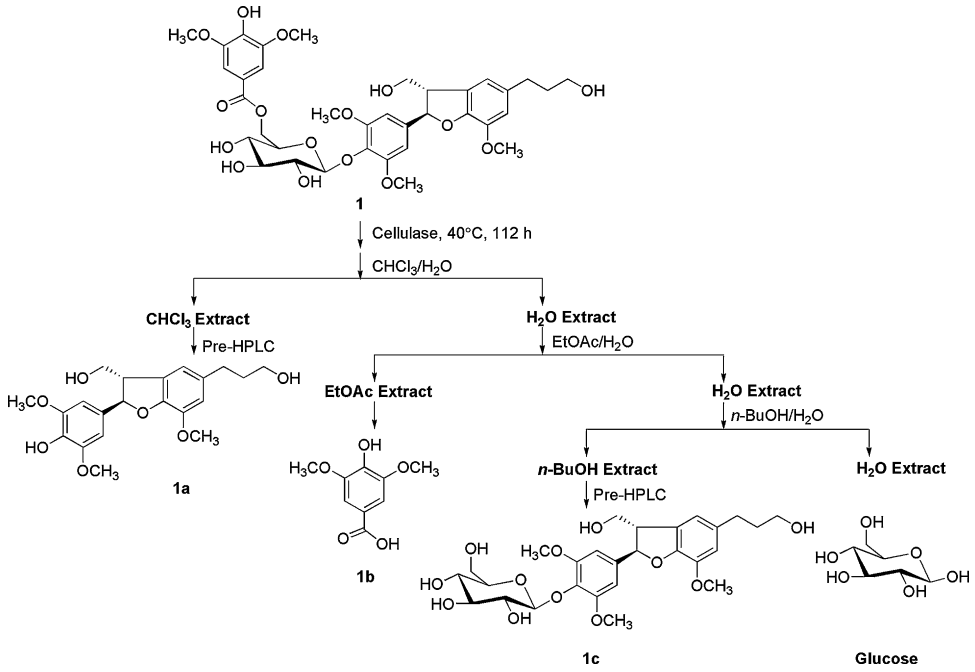


Fig. 2. ^{1}H–^{1}H COSY and key HMBC correlations of compound **1**.

Pittogoside B (**2**) was obtained as a yellow amorphous power. It exhibited $[M+Na]^+$ ion peak at *m/z* 543.1839 (calcd for 543.1837) in HRESI-MS, corresponding to the molecular formula $C_{26}H_{32}O_{11}$. The IR spectrum suggested the presence of hydroxyl group (3340 cm^{-1}),



Scheme 1. Enzymatic hydrolysis of compound **1**.

carbonyl group (1705 cm^{-1}) and aromatic ring (1604 and 1514 cm^{-1}). On enzymatic hydrolysis, **2** afforded D-glucose as a component sugar. The β-anomeric configuration for glucose was determined by its large $^{3}J_{H\text{-}1,H\text{-}2}$ coupling constant (7.8 Hz). In comparison of the NMR data of the aglycone of **2** with those of **1**, the signals due to ring A were superimposable, while some differences were observed for rings B and C. The absence of two methenyl carbons at δ 87.7 and 54.9, coupled with the appearance of two olefinic carbons at δ 155.6 and 131.9, suggested that **2** was a benzofuran lignan instead of dihydrobenzofuran lignan. In addition, the proton signals observed at δ 7.53 (1H, d, J = 1.8 Hz), 7.45 (1H, dd, J = 8.0, 1.8 Hz) and 6.95 (1H, d, J = 8.0 Hz) indicated the ABX substitution type of ring C. The placement of two methoxy groups was confirmed by the HMBC correlations from δ_H 4.02 (3′-OCH_3) to δ_C 144.7 (C-3′) and δ_H 3.99 (3-OCH_3) to δ_C 147.8 (C-3). Thus, the structure of the aglycone of **2** was determined to be 7-en-dihydrodehydrodiconiferyl alcohol (**2a**), which was obtained by enzymatic hydrolysis. The NMR data of **2a** was in accord with that of a known compound, 4-[3-(hydroxymethyl)-5-(3-hydroxypropyl)-7-methoxy-1-benzofuran-2-yl]-2-methoxyphenol, isolated from the bark of *Abies sachalinensis* (Wada et al., 2009). The connection of β-D-glucopyranose at C-9 of the aglycone was deduced by the HMBC correlation from δ_H 4.50 (Glc-H-1) to δ_C 60.3 (C-9). Based on the above evidences, the structure of **2** was established as 7-en-dihydrodehydrodiconiferyl alcohol-9-*O*-β-D-glucopyranoside.

Recent studies showed that lignan glycosides exhibited antioxidant activity (Yang et al., 2009; Sadhu et al., 2007; Zhang et al., 2008). Therefore, pittogosides A and B (**1** and **2**), and five lignan glycosides isolated previously from *P. glabratum* Lindl (Nie et al., 2011), (+)-lyoniresinol-3a-*O*-(6″-3-methoxy-4-hydroxybenzoyl)-β-D-glucopyranoside (**3**), lyoniresinol-3a-*O*-β-D-glucopyranoside (**4**), (+)-lyoniresinol-3a-*O*-(6″-3,5-dimethoxy-4-hydroxybenzoyl)-β-D-glucopyranoside (**5**), (−)-4-epi-lyoniresinol-3a-*O*-β-D-glucopyranoside (**6**) and syringaresinol-4,4′-*bis*-*O*-β-D-glucopyranoside (**7**), were evaluated for their antioxidant activities by 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical scavenging assay. Compounds **3**–**6** showed antioxidant activities with IC_{50} values of 35.3 ± 2.3, 35.7 ± 0.5, 47.4 ± 4.3 and 75.1 ± 7.7 μM, as compared to the activity of edaravone, which was used as a positive control (32.8 ± 2.8 μM). Two new compounds (**1** and **2**) and a known lignan glycoside (**7**) were inactive at 100 μM. In this experiment, the results indicated that antioxidant activities were closely related with the structural type of the lignans: aryltetralin lignans (**3**–**6**) showed antioxidant activities whereas neolignans (**1** and **2**) and furofuran lignan (**7**) showed no activities.

3. Experimental

3.1. General

The UV spectra were obtained with a Hitachi U-3000 spectrophotometer, whereas the IR spectra were measured with a Thermo Nicolet 670 FT-IR (by a KBr disk method) spectrometer. Specific rotation was measured on high-precision digital automatic polarimeter (Kerncher, Germany), while the CD spectra were recorded on an Applied Photophysics Chirascan spectropolarimeter. The ^{1}H and ^{13}C NMR spectra were recorded on Bruker Avance-600 spectrometer with TMS as the internal standard. The ESI-MS were taken on an Agilent Trap VL mass analyzer and the HRESI-MS were taken on a Thermo Scientific LTQ Orbitrap XL mass spectrometer. Preparative HPLC was performed on Agilent 1100 apparatus, equipped with a G1314A Variable Wavelength Detector and YMC-Pack RP-C18 column (150 mm × 20 mm, i.d.). Column chromatography was carried out using silica gel (200–300 mesh, Qingdao Marine Chemical Factory, Qingdao, China), Sephadex LH-20 (Amersham Biosciences, Sweden), Diaion HP-20 (20–60 mesh, Mitsubishi Chemical Holdings CO., Kyoto, Japan) and ODS (50 μm, YMC Co. Ltd., Kyoto, Japan).

3.2. Plant material

The roots of *P. glabratum* Lindl. were collected from Sichuan Province, People's Republic of China, in September 2009, and identified by one of the authors B. H. A voucher specimen (No. PG200909) has been deposited at the Department of Natural Products Chemistry, Institute of Materia Medica, Shandong Academy of Medical Sciences, Jinan, China.

3.3. Extraction and isolation

The air-dried roots of *P. glabratum* (12 kg) were extracted with 75% EtOH three times. Evaporation of the aqueous alcohol solution

under reduced pressure gave the EtOH extract (1065 g). The extract was suspended in H_2O and partitioned successively with EtOAc and *n*-BuOH. The EtOAc extract (91 g) was subjected to silica gel column chromatography (CC) and eluted with a gradient of $CHCl_3$–MeOH to give 7 fractions (Fr.A–Fr.G). Further isolation of Fr.D (28 g) was achieved by repeated silica gel CC, Sephadex LH-20 CC and preparative HPLC to give compound **1** (9 mg). The *n*-BuOH extract (198 g) was loaded on Diaion HP-20 column and eluted with 0%, 30%, 60% and 90% EtOH to obtain four fractions. The 30% EtOH eluate (39 g) was separated by silica gel CC with a gradient of $CHCl_3$–MeOH to give 10 fractions (Fr.I–Fr.X). Fr.VII (5 g) was fractionated by repeated silica gel, Sephadex LH-20, ODS CC and preparative HPLC to give compound **2** (5 mg).

Pittogoside A (**1**): White amorphous power. $[\alpha]_D^{20} = -9.0$ (*c* 0.9, MeOH:H_2O 4:6). IR (KBr): ν_{max}: 3340, 1705, 1599, 1515 cm^{-1}. UV λ_{max} (MeOH:H_2O 4:6) nm (log ε): 206 (4.28), 243 (sh, 3.39), 279 (3.44). HRESI-MS (positive) *m/z*: 755.2528 $[M+Na]^+$ (calcd for $C_{36}H_{44}O_{16}Na$ 755.2522). ^1H NMR (600 MHz, C_5D_5N) and ^{13}C NMR (150 MHz, C_5D_5N) data see Table 1.

Pittogoside B (**2**): Yellow amorphous powder, $[\alpha]_D^{20} = -22.1$ (*c* 0.5, MeOH). IR(KBr): ν_{max}: 3340, 1705, 1604, 1514 cm^{-1}. UV λ_{max} (MeOH) nm (log ε): 216 (4.21), 306 (4.04). HRESI-MS (positive) *m/z*: 543.1839 $[M+Na]^+$ (calcd for $C_{26}H_{32}O_{11}Na$ 543.1837). ^1H NMR (600 MHz, CD_3OD) and ^{13}C NMR (150 MHz, CD_3OD) data see Table 1.

3.4. Enzymatic hydrolysis of compounds 1 and 2

A solution of **1** (4.8 mg) and **2** (3.1 mg) in 1 ml H_2O was treated with cellulase (Sigma Chemical Co., 20 mg and 15 mg) and then the mixture was stirred at 40 °C for 112 h and 96 h. The reaction mixture was suspended in H_2O, then extracted successively with $CHCl_3$, EtOAc and BuOH for **1** and extracted with EtOAc for **2**. The organic layers were evaporated or purified by pre-HPLC to give **1a** (1.0 mg), **1b** (0.3 mg), **1c** (0.2 mg) and **2a** (0.1 mg), respectively. The aqueous layers of **1** and **2** were concentrated under reduced pressure to give the sugar fractions.

5-Methoxy-dihydrodehydrodiconiferyl alcohol (**1a**): UV λ_{max} (MeOH) nm (log ε): 208 (4.36), 242 (sh, 3.60), 284 (3.16). CD ($c = 1.03 \times 10^{-4}$ mol/l, MeOH) $\Delta\varepsilon$ −0.61 (244 nm). ESI-MS (positive) *m/z*: 413 $[M+Na]^+$. ^1H NMR (600 MHz, CD_3OD) δ: 6.64 (2H, s, H-2, 6), 6.70 (1H, s, H-6′), 6.69 (1H, s, H-2′), 5.46 (1H, d, *J* = 6.6 Hz, H-7), 3.43 (1H, m, H-8), 3.81 (1H, dd, *J* = 11.4, 6.0 Hz, H-9a), 3.73 (1H, dd, *J* = 11.4, 7.8 Hz, H-9b), 2.59 (2H, t, *J* = 7.8 Hz, H-7′), 1.78 (2H, m, H-8′), 3.53 (2H, t, *J* = 6.6 Hz, H-9′), 3.82 (3H, s, 3′-OCH_3), 3.77 (6H, s, 3, 5-OCH_3).

Syringic acid (**1b**): ESI-MS (negative) *m/z*: 197 $[M-H]^-$. ^1H NMR (600 MHz, CD_3OD) δ: 7.32 (2H, s, H-2, 6), 3.88 (6H, s, 3, 5-OCH_3).

5-Methoxy-dihydrodehydrodiconiferyl alcohol-4-*O*-β-D-glucopyranoside (**1c**): UV λ_{max} (MeOH) nm (log ε): 208 (4.15), 240 (sh, 3.38), 282 (2.75). CD ($c = 2.41 \times 10^{-4}$ mol/l, MeOH) $\Delta\varepsilon$ −0.21 (248 nm). ESI-MS (positive) *m/z*: 575 $[M+Na]^+$. ^1H NMR (600 MHz, CD_3OD) δ: 6.76 (2H, s, H-2, 6), 6.77 (1H, s, H-6′), 6.73 (1H, s, H-2′), 5.59 (1H, d, *J* = 6.0 Hz, H-7), 3.47 (1H, m, H-8), 3.89 (1H, dd, *J* = 11.0, 4.8 Hz, H-9a), 3.78 (1H, dd, *J* = 11.0, 7.8 Hz, H-9b), 3.90 (3H, s, 3′-OCH_3), 3.84 (6H, s, 3, 5-OCH_3), 2.64 (2H, t, *J* = 7.2 Hz, H-7′), 1.83 (2H, m, H-8′), 3.58 (2H, t, *J* = 6.6 Hz, H-9′), 4.90 (1H, overlapped, Glc-H-1), 3.78 (1H, dd, *J* = 12.0, 2.4 Hz, Glc-H-6a), 3.67 (1H, dd, *J* = 12.0, 5.4 Hz, Glc-H-6b), 3.30–3.35 (4H, overlapped, Glc-H-2, 3, 4, 5).

7-en-Dihydrodehydrodiconiferyl alcohol (**2a**): ESI-MS (positive) *m/z*: 381 $[M+Na]^+$. ^1H NMR (600 MHz, CD_3OD) δ: 7.49 (1H, d, *J* = 1.8 Hz, H-2), 7.36 (1H, dd, *J* = 8.0, 1.8 Hz, H-6), 6.94 (1H, d, *J* = 8.0 Hz, H-5), 7.14 (1H, s, H-6′), 6.77 (1H, s, H-2′), 4.85 (2H, s, H-9), 4.03 (3H, s, 3′-OCH_3), 3.97 (3H, s, 3-OCH_3), 3.63 (2H, t, *J* = 6.6 Hz, H-9′), 2.80 (2H, t, *J* = 7.8 Hz, H-7′), 1.93 (2H, m, H-8′).

3.5. Absolute configuration of sugars in compounds 1 and 2

The sugar fraction obtained by enzymatic hydrolysis was dissolved in 1 ml H_2O, to which (*S*)-(−)-α-methylbenzylamine (17 μl) and $NaBH_3CN$ (8 mg) in EtOH (1 ml) was added. After being stirred at 40 °C for 4 h followed by addition of glacial acetic acid (0.2 ml) and evaporated to dryness, the resulting solid was acetylated with acetic anhydride (0.3 ml) in pyridine (0.3 ml) for 24 h at room temperature. After evaporation, H_2O (1 ml) was added to the residue and the solution was passed through a Cleanert C_{18}-SPE column (Agela) with H_2O, 20% and 50% CH_3CN (15, 15 and 10 ml) as solvents. The 50% CH_3CN eluate, the 1-[(*S*)-*N*-acetyl-α-methylbenzylamino]-1-deoxyglucitol acetate derivative, was then analyzed by HPLC under the following conditions: Column, Agilent SB-C_{18} (4.6 mm × 250 mm, 5 μm); solvent, 40% CH_3CN; flow rate, 0.8 ml/min; detection, DAD detection, 230 nm. The identification of D-glucose or L-glucose present in the sugar faction was carried out by a comparison of retention times of their derivatives with those of the authentic samples: t_R (min) 22.36 (derivative of D-glucose) and 20.67 (derivative of L-glucose). D-Glucose was detected from **1** and **2**.

Acknowledgement

This project was supported by Key Laboratory for Rare and Uncommon Diseases of Shandong Province.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.phytol.2012.01.003.

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