Fortuneanosides G—L, Dibenzofuran Glycosides from the Fruit of *Pyracantha fortuneana*

Yi DAI,[a] Guang-Xiong ZHOU,[a] Hiroshi KURIHARA,[a] Wen-Cai YE,[a] and Xin-Sheng YAO*,[a,b]

[a] *Institute of Traditional Chinese Medicine & Natural Products, College of Pharmacy, Jinan University; Guangzhou 510632, China: and* [b] *Department of Natural Products Chemistry, Shenyang Pharmaceutical University; Shenyang 110016, China.* Received September 14, 2007; accepted November 27, 2007

Six new dibenzofuran glycosides, fortuneanosides G (1), H (2), I (3), J (4), K (5), and L (6), were isolated from the fruit of *Pyracantha fortuneana* (MAXIM) LI. Their structures were determined to be 3,7-dihydroxy-2,4-dimethoxy-dibenzofuran 7-*O*-β-D-glucopyranoside, 3,7-dihydroxy-2,4-dimethoxy-dibenzofuran 7-*O*-(α-L-rhamnopyranosyl)-(1—6)-β-D-glucopyranoside, 3,6-dihydroxy-2,4-dimethoxy-dibenzofuran 6-*O*-β-D-glucopyranoside, 2,4-dimethoxy-3,6,9-trihydroxy-dibenzofuran 6-*O*-β-D-glucopyranoside, 3,9-dihydroxy-2,4-dimethoxy-dibenzofuran 3-*O*-β-D-glucopyranoside, and 2-methoxy-3,4,9-trihydroxy-dibenzofuran 4-*O*-β-D-glucopyranoside based on spectroscopic analysis. Fortuneanosides G—J showed more potent tyrosinase-inhibitory activity than arbutin.

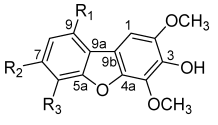
Key words *Pyracantha fortueneana*; dibenzofuran glycoside; tyrosinase-inhibitory activity

Melanin is a heterogeneous polyphenol-like biopolymer secreted by the melanocytes in the basal layer of skin.[1] The type and amount of melanin and its distribution determine skin color.[2] Tyrosinase (EC.1.14.18.1), a copper-containing enzyme widely distributed in nature, is a key enzyme in the biosynthesis of melanin.[3] Thus tyrosinase inhibitors may be clinically used for the treatment of some skin disorders associated with melanin hyperpigmentation and are also important in cosmetics for skin-whitening effects.[4] Our previous investigation searching tyrosinase-inhibitory active constituents from *Pyracantha fortuneana* (MAXIM) LI led to the isolation of five new biphenyl glycosides, fortuneanosides A—E.[5] The continuous study of this plant revealed six dibenzofuran glycosides. Their structures were elucidated by concerted application of 1D and 2D NMR experiments, and their tyrosinase-inhibitory activities were evaluated *in vitro*.

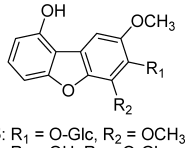
Results and Discussion

The 60% (v/v) EtOH extract of the dried fruit of *P. fortuneana* was subjected to column chromatography, followed by preparative reverse-phase HPLC. Six new dibenzofuran glycosides, fortuneanosides G (**1**), H (**2**), I (**3**), J (**4**), K (**5**), and L (**6**), were obtained from the fractions with tyrosinase-inhibitory activity. The structures of compounds **1**—**6** were elucidated from the analysis of extensive 1D and 2D NMR spectra.

Fortuneanoside G (**1**) was obtained as a pale yellow gum. The molecular formula was established to be $C_{20}H_{22}O_{10}$ based on high resolution electrospray ionization mass spectrocopy (HR-ESI-MS) (*m*/*z* 445.1113 $[C_{20}H_{22}O_{10}Na]^+$). The ^{1}H-NMR spectrum of **1** showed typical signals of a 1,2,4-trisubstituted benzene ring [δ 7.29 (1H, d, J=6.2 Hz), 7.28 (1H, d, J=2.8 Hz), 7.06 (1H, dd, J=6.2, 2.8 Hz)], a singlet (δ 7.49, 1H) arising from a pentasubstituted benzene ring, and two singlet signals due to *O*-methyl groups (δ 3.98, 3.88). The remaining signals at δ 3.24, 3.35, 3.38, 3.44, 3.49/3.70, and 5.06 correlated with the carbon signals at δ 69.7 (C-4′), 76.8 (C-3′), 77.1 (C-5′), 73.4 (C-2′), 60.6 (C-6′), and 100.7(C-1′) in the hetero-nuclear single quantum coherence (HSQC) spectrum, respectively. The results suggested the presence of a glucose residue in the structure of **1**. Acid hydrolysis of **1** further confirmed the structural elucidation. The absolute configuration of the glucose was demonstrated to be the D configuration using the method of Hara *et al.*[6] The aromatic protons at δ 7.29, 7.28, and 7.06 were assigned as H-9, H-6, and H-8 on the basis of the splitting pattern and correlation spectro scopy (COSY) correlations. The hetero multiple bonding connectivity (HMBC) correlations of H-6/C-8 (δ 109.0), H-9/C-8, and H-8/C-6 (δ 105.3) further confirmed their location. The *O*-linked aromatic quaternary carbon signals at δ 152.2 and 156.4 both correlated with H-9, and the former also correlated with H-8. Thus they were assigned as C-7 and C-5a, respectively. The rotational nuclear Overhauser effect spectroscopy (ROESY) correlation between the *O*-methyl signal at δ 3.88 and H-1 (δ 7.49) revealed a methoxy group located at C-2 (δ 145.9). The *O*-linked aromatic quaternary carbon signals at δ 138.9 and 142.3 were assigned as C-3 and C-4a according to their HMBC correlations with H-1. The chemical shifts of the *m*-substituted aromatic quaternary carbons C-3 and C-4a were both less than 150, indicating an *O*-substituted aromatic carbon at C-4. Therefore, the remaining *O*-linked quaternary carbon signal at δ 132.8 was assigned as C-4. The methoxy group at δ 3.98 was located at C-4 according to the HMBC correlation. Both aromatic quaternary carbon signals at δ 113.4 and 114.6 correlated with H-1 and H-9, and the latter also correlated with H-8, suggesting that they were attributed to C-9b and C-9a, by which connected by two aromatic rings. The location of the glucose residue was established to be at C-7 according to the HMBC cross-peak between H-1′ (δ 5.06) and C-7. The molecular formula indicates that C-4a and C-5a are connected with an oxygen atom, and a hydroxyl group is substi-



1: $R_1 = R_3 = H$, R_2 = O-Glc
2: $R_1 = R_3 = H$, R_2 = O-Glc-Rha
3: $R_1 = R_2 = H$, R_3 = O-Glc
4: R_1 = OH, $R_2 = H$, R_3 = O-Glc



5: R_1 = O-Glc, $R_2 = OCH_3$
6: R_1 = OH, R_2 = O-Glc

* To whom correspondence should be addressed. e-mail: yaoxinsheng@vip.tom.com

tuted at C-3. Therefore **1** was determined to be 2,4-dimethoxy-3-hydroxy-dibenzofuran-7-*O*-β-D-glucopyranoside.

Fortuneanoside H (**2**) was isolated as a pale yellow gum and had the molecular formula $C_{26}H_{32}O_{14}$ based on the results of HR-ESI-MS. The ^{1}H- and ^{13}C-NMR spectra of **2** were similar to those of **1** (Table 1), expect for the signals in the sugar region. Acid hydrolysis of **2** gave D-glucose and L-rhamnose in a ratio of 1 : 1, which was further confirmed by the ^{13}C-NMR spectrum. The rhamnose residue was located at C-6′ (δ 66.7) of the glucose residue due to the obvious glycosylation shift of C-6′. The linkage of the glucose residue was located at C-7 (δ 152.1) according to the HMBC correlation between H-1′ (δ 5.02) and C-7. Thus **2** was elucidated to be 2,4-dimethoxy-3-hydroxy-dibenzofuran-7-*O*-(α-L-rhamnopyranosyl)-(1—6)-β-D-glucopyranoside.

Fortuneanoside I (**3**), obtained as a pale yellow gum, had the molecular formula $C_{20}H_{22}O_{10}$ based on the results of HR-ESI-MS. The ^{1}H-NMR spectrum showed the presence of a 1,2,3-trisubstituted benzene ring [δ 7.59 (1H, d, J=7.6 Hz), 7.22 (1H, dd, J=7.6, 7.6 Hz), 7.13 (1H, d, J=7.6 Hz)] and a pentasubstitued benzene ring (δ 7.39, 1H). The *O*-methyl signals at δ 3.99 and 3.88 suggested that there were two methoxy groups in **3**. The remaining signals in the ^{1}H-NMR spectrum, together with the cross-peaks in the HSQC spectrum, revealed the presence of a glucose moiety. The acid hydrolysis of **3** further confirmed this elucidation. The aromatic proton signals at δ 7.59, 7.22, and 7.13 were respectively assigned to H-9, H-8, and H-7, according to the splitting pattern and their successive correlations in the COSY spectrum. The *O*-linked aromatic quaternary carbons at δ 143.9 and 142.7 both correlated with H-7. The former also correlated with H-9, while the latter correlated with H-8. They were accordingly attributed to C-5a and C-6. The methoxy group at δ 3.88 was located at C-2 (δ 146.3), as it correlated with H-1 (δ 7.39) in the ROESY spectrum. The HMBC correlations of H-1/δ 139.5 and H-1/δ 142.7 indicated that these two aromatic quaternary carbons were attributed to C-3 and C-4a, respectively. The remaining *O*-linked carbon signal at δ 133.2 was then assigned as C-4 due to the obvious upfield shifts of C-3 and C-4a. The HMBC correlation between *O*-methyl at δ 3.99 and C-4 suggested that the methoxy group was attached to C-4. The linkage of the glucose residue was established to be at C-6, as the anomeric proton signal at δ 5.18 correlated with C-6 in the HMBC spectrum. Thus **3** was deduced to be 2,4-dimethoxy-3-hydroxy-dibenzofuran-6-*O*-β-D-glucopyranoside.

Fortuneanoside J (**4**) was obtained as a pale yellow gum. The molecular formula was established to be $C_{20}H_{22}O_{11}$ using HR-ESI-MS. The ^{1}H-NMR data of **4** were similar to those of **3** but showed one less aromatic proton signal, suggesting that the 1,2,3-trisubstituted benzene ring in **3** was replaced by a 1,2,3,4-tetrasubstituted benzene ring [δ 6.94 (1H, d, J=8.7 Hz), 6.59 (1H, d, J=8.7 Hz)] in **4**. These aromatic protons were respectively assigned as H-7 and H-8 according to their HMBC correlations. The glucose residue was located at C-6 (δ 135.6) due to the HMBC correlation of H-1′ (δ 4.96)/C-6. Therefore **4** was determined to be 2,4-dimethoxy-3,9-dihydroxy-dibenzofuran-6-*O*-β-D-glucopyranoside.

Fortuneanoside K (**5**), obtained as a pale yellow gum, had the molecular formula $C_{20}H_{22}O_{10}$ based on HR-ESI-MS. The ^{1}H-NMR spectrum showed typical signals of a 1,2,3-trisubstituted benzene ring [δ 7.23 (1H, dd, J=8.0, 8.0 Hz), 7.07 (1H, d, J=8.0 Hz), 6.77 (1H, d, J=8.0 Hz)], a singlet (δ 7.33, 1H) from a pentasubstituted aromatic moiety, and two singlet signals due to *O*-methyl groups (δ 4.05, 3.86). The remaining signals in the ^{1}H-NMR spectrum and their cross-peaks in the HSQC spectrum revealed the presence of a glucose residue. This was further confirmed by the acid hydrolysis and gas chromatographic analysis. The aromatic protons at δ 7.23, 7.07, and 6.77 were assigned as H-6, H-7, and H-8, respectively, due to the splitting pattern and their successive correlations in the COSY spectrum. Both of the two *O*-linked aromatic quaternary carbons at δ 154.1 and 157.3 correlated with H-7 and were accordingly attributed to C-5a and C-9. The obvious upfield shifts of the other *O*-linked aromatic carbons (δ 136.6, 138.5, 141.6, 149.8) indicated that they were all at the *o*- and *p*-substituted position of the others. They were assigned as C-3, C-4, C-4a, and C-2 on the basis of the HMBC correlations. The location of the two *O*-methyl signals at δ 4.05 and 3.86 were determined to be at C-4 and C-2 according to the HMBC correlations. The ROESY correlation between the *O*-methyl signal at δ 3.86 and H-1 (δ 7.33) further confirmed the elucidation. Both of the methoxy groups correlated with the anomeric proton at δ 4.98 in the ROESY spectrum, suggesting that the glucose residue was attached at C-3. Thus **5** was deduced to be 2,4-dimethoxy-9-hydroxy-dibenzofuran-3-*O*-β-D-glucopyranoside.

Fortuneanoside L (**6**), isolated as a pale yellow gum, had the molecular formula $C_{19}H_{20}O_{10}$ based on HR-ESI-MS. The ^{1}H- and ^{13}C-NMR data of **6** were similar to those of **5** except for the loss of a methoxy group. Acid hydrolysis and gas

Table 1. ^{13}C-NMR Data (δ) for Compounds **1**—**6** (in DMSO-d_6, 100 MHz)

Position	**1**	**2**	**3**	**4**	**5**	**6**
1	100.2 d	100.3 d	97.8 d	99.0 d	100.0 d	99.7 d
2	145.9 s	146.0 s	146.3 s	146.0 s	149.8 s	145.4 s
3	138.9 s	139.0 s	139.5 s	138.8 s	136.6 s	138.2 s
4	132.8 s	132.8 s	133.2 s	133.1 s	138.5 s	130.2 s
4a	142.3 s	142.3 s	142.7 s	142.2 s	141.6 s	141.6 s
5a	156.4 s	156.3 s	143.9 s	145.6 s[a)]	154.1 s[a)]	152.7 s[a)]
6	105.3 d	105.5 d	142.7 s	135.6 s	102.0 d	102.3 d
7	152.2 s	152.1 s	111.7 d	113.4 d	127.5 d	127.5 d
8	109.0 d	109.4 d	123.4 d	107.9 d	108.8 d	108.5 d
9	126.2 d	126.2 d	113.1 d	147.1 s[a)]	157.3 s[a)]	156.9 s[a)]
9a	114.6 s	114.7 s	126.1 s	114.2 s	112.2 s	112.4 s
9b	113.4 s	113.4 s	112.1 s	113.4 s	119.2 s	123.3 s
Glc-1′	100.7 d	100.9	100.2 d	101.5 d	102.8 d	103.6 d
2′	73.4 d	73.4	73.2 d	73.3 d	74.1 d	73.8 d
3′	76.8 d	75.6	76.8 d	76.8 d	76.5 d	76.3 d
4′	69.7 d	70.1	69.6 d	69.7 d	70.0 d	69.6 d
5′	77.1 d	76.8	77.1 d	77.1 d	77.3 d	77.3 d
6′	60.6 t	66.7	60.6 t	60.7 t	60.9 t	60.6 t
Rha-1″		100.7				
2″		70.4				
3″		70.7				
4″		72.0				
5″		68.4				
6″		17.8				
2-OCH_3	56.5 q	56.5	56.5 q	56.4 q	56.9 q	56.4 q
4-OCH_3	60.4 q	60.4	60.5 q	60.4 q	60.8 q	

a) Could be exchanged each other.

Table 2. Inhibitory Activity of Compounds **1**—**6** to Tyrosinase

Compound	**1**	**2**	**3**	**4**	**5**	**6**	Arbutin
IC_{50} [a] (mM)	0.08	0.12	0.19	0.14	>5	>5	0.23

a) The results are from the three concurrent readings and each S.D. was usually within 2% of the mean.

chromatographic analysis showed the presence of a glucose residue, and the D configuration was confirmed by on the comparison of the gas chromatography retention time of the derivative with those of standard monosaccharides. The methoxy group at δ 3.86 was located at C-2 (δ 145.4) according to the ROESY correlation between the *O*-methyl and H-1 (δ 7.29). The linkage of the glucose residue was established to be at C-4 (δ 130.2) due to the obvious glycosylation shift of C-4. Therefore **6** was elucidated to be 2-methoxy-3,9-dihydroxy-dibenzofuran-4-*O*-β-D-glucopyranoside.

The tyrosinase-inhibitory activities of compounds **1**—**6** were evaluated *in vitro* using arbutin as a positive control. The results, which are listed in Table 2, showed that compounds **1**, **2**, **3**, and **4** are more potent than arbutin. However, compounds **5** and **6** had no inhibitory activities against tyrosinase. Combined with our preliminary investigation, the consecutive polyphenolic hydroxyl groups might contribute to the inhibitory activity, and the location of the monosaccharide could slightly affect the activity. The inhibitory activity might arise from the chelation to copper in the active site of tyrosinase.[7,8] Further assays are needed to confirm this assumption.

Experimental

General Procedure Optical rotations were measured on a JASCO P-1020 digital polar meter. UV spectra were recorded on a JASCO V-550 UV/Vis spectrometer. IR spectra were obtained using a JASCO FT/IR-480 plus spectrometer. ESI-MS spectra were taken on a FINIGAN LCQ Advantage MAX mass spectrometer. HR-ESI-MS spectra were acquired using a Micromass Q-TOF mass spectrometer. 1D and 2D NMR spectra were measured with a Bruker AV-400 spectrometer using DMSO-d_6 solution.

Plant Material The plant was collected on Mount Qinling, Shanxi province, China, in November 2003, and identified as *P. fortuneana*. A voucher specimen (20031202) is deposited in the Institute of Traditional Chinese Medicine and Natural Products, Jinan University, Guangzhou, China.

Extraction and Isolation The air-dried fruit (5.0 kg) of *P. fortuneana* was refluxed twice with 60% (v/v) aqueous EtOH (30 l) for 2 h each time. After evaporation to dryness under a vacuum, the residue was suspended in H_2O and then successively partitioned with *n*-hexane, $CHCl_3$, EtOAc, and *n*-BuOH to afford 18.4, 36.1, 30.1, and 126.6 g of extracts, respectively. The open silica gel column chromatography of the *n*-BuOH extract, eluted with $CHCl_3$–MeOH–H_2O (20 : 1 : 0 to 5 : 5 : 1), gave 15 fractions. Fraction 3 (2.36 g, eluted with $CHCl_3$–MeOH 10 : 1) showed inhibitory activity against tyrosinase, and further separation was performed using reverse-phase column chromatography eluted with MeOH–H_2O in a gradient, yielding six fractions (A1—A6). Fraction A3 (eluted with 60% MeOH–H_2O) was then subjected to column chromatography on HW-40 eluted with gradient MeOH–H_2O to yield six subfractions. Compounds **1** (2.4 mg) and **3** (2.4 mg) were obtained from the fourth subfraction (eluted with 60% MeOH–H_2O) after purification by preparative HPLC with 25% MeCN–H_2O. Fraction 4 (4.47 g, eluted with $CHCl_3$–MeOH 4 : 1), another tyrosinase inhibitor, was also fractionated on a reverse-phase column eluted with MeOH–H_2O in gradient to yield 14 fractions (B1—B14). Column chromatography on HW-40 of fraction B9 (eluted with 60% MeOH–H_2O) eluted with gradient MeOH–H_2O gave six subfractions. Compounds **1** (4.4 mg) and **5** (5.0 mg) were obtained from the third (eluted with 60% MeOH–H_2O) subfraction, and compounds **4** (1.6 mg) and **6** (1.8 mg) were obtained from the fourth (eluted with 60% MeOH–H_2O) subfraction after purification by preparative HPLC with 15—20% MeCN–H_2O (Synergi Fusion-RP 8 column 21.2×250 mm, Phenomenex). In addition, fraction B3 (eluted with 30% MeOH–H_2O) was also separated on HW-40 column chromatography, and compound **2** (4.9 mg) was obtained from the third subfraction (eluted with 60% MeOH–H_2O) by repeated preparative HPLC with 20% MeCN–H_2O (Synergi Fusion-RP 8 column 21.2×250 mm, Phenomenex).

Acid Hydrolysis and Gas Chromatographic Analysis Acid hydrolysis of **1**—**6** was performed using the method of Hara *et al.*[6] to determine the absolute configuration of the monosaccharide. One milligram of the compound, *e.g.*, **1**, was hydrolyzed with HCl 1 M for 2 h at 80 °C. The mixture was evaporated to dryness under a vacuum, and then the residue was dissolved in H_2O and extracted with EtOAc. The aqueous layer was concentrated *in vacuo* to give a residue that was dissolved in dry pyridine, to which was added L-cysteine methyl ester hydrochloride (Sigma, U.S.A.). The reaction mixture was heated for 2 h at 60 °C and concentrated to dryness with N_2 gas. To the residue was added trimethylsilyl imidazole (Fluka, U.S.A.), followed by heating for 1 h at 60 °C. The residue was extracted with hexane and H_2O, and the organic layer was analyzed using gas chromatography: column, AT-SE-30 (0.5 μ×0.32 mm×30 m); detector, FID; column temperature, 220 °C; detector temperature, 270 °C; injector temperature, 270 °C; and carrier gas, N_2. One peak of the derivatives of **1** was observed at t_R 29.58 min (D-Glc). The standard monosaccharides, such as L-rhamnose, D-glucose, L-glucose, and D-galactose (Sigma, U.S.A.), were subjected to the same reaction and gas chromatographic analysis under the same conditions. The peaks of the mixed standard monosaccharide derivatives were recorded at t_R 18.71 (L-Rha), 29.59 (D-Glc), 30.98 (L-Glc), and 31.80 min (D-Gal). Following this procedure, **2**—**6** were also subjected to acid hydrolysis and gas chromatographic analysis. Two peaks of the derivatives of **2** were observed at t_R 18.60 (L-Rha) and 29.43 min (D-Glc), while **3**—**6** gave one peak with the retention time 29.4—29.6 min (D-Glc).

Assay of Tyrosinase-Inhibitory Activity This assay was carried out according to the procedure of Mason and Peterson[9] with slight modifications.[5]

Fortuneanoside G (**1**): Pale yellow gum; $[\alpha]_D^{25}$ −39.9° (*c*=1.00, MeOH); UV λ_{max} (MeOH) nm (log ε): 222 (4.37), 264 (3.96), 287 (3.99), 304 (sh) (3.82), 315 (3.86); IR (KBr) cm^{-1}: 3389, 1603, 1468, 1427, 1077, 1025; ^{1}H-NMR (DMSO-d_6, 400 MHz) δ: 7.49 (1H, s, H-1), 7.29 (1H, br d, *J*=6.2 Hz, H-9), 7.28 (1H, d, *J*=2.8 Hz, H-6), 7.06 (1H, dd, *J*=6.2, 2.8 Hz, H-8), 5.06 (1H, d, *J*=7.6 Hz, H-1′), 3.98 (3H, s, 4-OCH_3), 3.88 (3H, s, 2-OCH_3), 3.70 (1H, m, H-6′a), 3.49 (1H, m, H-6′b), 3.44 (1H, m, H-2′), 3.38—3.24 (overlapped in HDO, H-5′, H-3′, H-4′); ^{13}C-NMR (DMSO-d_6, 100 MHz), see Table 1; ESI-MS *m/z* 445 $[M+Na]^+$, 867 $[2M+Na]^+$; HR-ESI-MS *m/z* 445.1113 (Calcd for $C_{20}H_{22}O_{10}Na$: 445.111).

Fortuneanoside H (**2**): Pale yellow gum; $[\alpha]_D^{25}$ −34.7° (*c*=0.49, MeOH); UV λ_{max} (MeOH) nm (log ε): 207 (4.58), 264 (3.95), 287 (3.98), 315 (3.84); IR (KBr) cm^{-1}: 3407, 1605, 1070; ^{1}H-NMR (DMSO-d_6, 400 MHz) δ: 7.63 (1H, s, H-1), 7.30 (1H, br d, *J*=6.0 Hz, H-9), 7.29 (1H, d, *J*=3.2 Hz, H-6), 7.05 (1H, dd, *J*=6.0, 3.2 Hz, H-8), 5.02 (1H, d, *J*=7.8 Hz, H-1′), 4.57 (1H, br s, H-1″), 3.99 (3H, s, 4-OCH_3), 3.89 (3H, s, 2-OCH_3), 3.90 (1H, m, H-6′a), 3.62 (1H, m, H-2″), 3.53 (1H, m, H-3′), 3.49 (1H, o, H-2′), 3.48 (1H, o, H-3″), 3.47 (1H, o, H-5″), 3.46 (1H, o, H-6′b), 3.35—3.18 (overlapped in HDO, H-5′, H-4′, H-4″), 1.12 (3H, d, *J*=6.2 Hz, H-6″) ; ^{13}C-NMR (DMSO-d_6, 100 MHz), see Table 1; ESI-MS *m/z* 591 $[M+Na]^+$; HR-ESI-MS *m/z* 591.1719 (Calcd for $C_{26}H_{32}O_{14}Na$: 591.1690).

Fortuneanoside I (**3**): Pale yellow gum; $[\alpha]_D^{25}$ −21.2° (*c*=1.21, MeOH); UV λ_{max} (MeOH) nm (log ε): 208 (4.56), 262 (4.05), 290 (4.09), 314 (sh) (3.90); IR (KBr) cm^{-1}: 3390, 1602, 1077; ^{1}H-NMR (DMSO-d_6, 400 MHz) δ: 7.59 (1H, d, *J*=7.6 Hz, H-9), 7.39 (1H, s, H-1), 7.22 (1H, dd, *J*=7.6, 7.6 Hz, H-8), 7.13 (1H, d, *J*=7.6 Hz, H-7), 5.18 (1H, d, *J*=7.4 Hz, H-1′), 3.99 (3H, s, 4-OCH_3), 3.88 (3H, s, 2-OCH_3), 3.67 (1H, m, H-6′a), 3.48 (1H, m, H-6′b), 3.37—3.23 (overlapped in HDO, H-2′, H-5′, H-3′, H-4′); ^{13}C-NMR (DMSO-d_6, 100 MHz), see Table 1; ESI-MS *m/z* 445 $[M+Na]^+$; HR-ESI-MS *m/z* 445.1115 (Calcd for $C_{20}H_{22}O_{10}Na$: 445.1111).

Fortuneanoside J (**4**): Pale yellow gum; $[\alpha]_D^{25}$ −18.3° (*c*=0.80, MeOH); UV λ_{max} (MeOH) nm (log ε): 204 (4.38), 268 (3.99), 322 (3.80); IR (KBr) cm^{-1}: 3405, 1603, 1075; ^{1}H-NMR (DMSO-d_6, 400 MHz) δ: 7.23 (1H, s, H-1), 6.94 (1H, d, *J*=8.7 Hz, H-7), 6.59 (1H, d, *J*=8.7 Hz, H-8), 4.96 (1H, d, *J*=7.2 Hz, H-1′), 3.98 (3H, s, 4-OCH_3), 3.84 (3H, s, 2-OCH_3), 3.65 (1H, m, H-6′a), 3.47 (1H, m, H-6′b), 3.38—3.20 (overlapped in HDO, H-2′, H-5′, H-3′, H-4′); ^{13}C-NMR (DMSO-d_6, 100 MHz), see Table 1; ESI-MS *m/z* 461 $[M+Na]^+$; HR-ESI-MS *m/z* 461.1071 (Calcd for $C_{20}H_{22}O_{11}Na$: 461.1060).

Fortuneanoside K (**5**): Pale yellow gum; $[\alpha]_D^{25}$ −20.8° (*c*=0.99, MeOH); UV λ_{max} (MeOH) nm (log ε): 222 (4.46), 264 (4.09), 281 (sh) (3.99), 318 (3.87); IR (KBr) cm^{-1}: 3406, 1601, 1461, 1426, 1069, 1030; ^{1}H-NMR (DMSO-d_6, 400 MHz) δ: 7.33 (1H, s, H-1), 7.23 (1H, dd, *J*=8.0, 8.0 Hz, H-7), 7.07 (1H, d, *J*=8.0 Hz, H-6), 6.77 (1H, d, *J*=8.0 Hz, H-8), 4.98 (1H, d,

J=7.3 Hz, H-1′), 4.05 (3H, s, 4-OCH_3), 3.86 (3H, s, 2-OCH_3), 3.61 (1H, d, J=10.8 Hz, H-6′a), 3.42 (1H, m, H-6′b), 3.24—3.18 (overlapped in HDO, H-2′, H-5′, H-3′, H-4′); ^{13}C-NMR (DMSO-d_6, 100 MHz), see Table 1; ESI-MS m/z 445 $[M+Na]^+$; HR-ESI-MS m/z 445.1139 (Calcd for $C_{20}H_{22}O_{10}Na$: 445.1111).

Fortuneanoside L (**6**): Pale yellow gum; $[\alpha]_D^{25}$ −19.9° (c=0.70, MeOH); UV λ_{max} (MeOH) nm (log ε): 211 (4.51), 265 (4.08), 285 (sh) (3.99), 317 (3.98); IR (KBr) cm^{-1}: 3407, 1605, 1384, 1074, 1026; ^{1}H-NMR (DMSO-d_6, 400 MHz) δ: 7.29 (1H, s, H-1), 7.16 (1H, t, J=8.0 Hz, H-7), 7.03 (1H, d, J=8.0 Hz, H-6), 6.74 (1H, d, J=8.0 Hz, H-8), 5.12 (1H, d, J=7.2 Hz, H-1′), 3.86 (3H, s, 2-OCH_3), 3.60 (1H, d, J=10.0 Hz, H-6′a), 3.49 (1H, m, H-6′b), 3.37—3.21 (overlapped in HDO, H-2′, H-4′, H-3′, H-5′); ^{13}C-NMR (DMSO-d_6, 100 MHz), see Table 1; ESI-MS m/z 431 $[M+Na]^+$; HR-ESI-MS m/z 431.0952 (Calcd for $C_{19}H_{20}O_{10}Na$: 431.0954).

Acknowledgements The authors are grateful to Professor Yang Ye, Shanghai Institute of Materia Medica of Chinese Academy of Science for HR-ESI-Q-TOF-MS experiments and to Dr. Qian Li, Institute of Traditional Chinese Medicine and Natural Products of Jinan University, for the measuring all NMR spectra.

References

1) Riley P. A., *Int. J. Biochem. Cell Biol.*, **29**, 1235—1239 (1997).
2) Kim Y. J., Yama H., *Cell. Mol. Life Sci.*, **62**, 1707—1723 (2005).
3) Van Gelder C. W. G., Flurkey W. H., Wichers H. J., *Phytochemistry*, **45**, 1309—1323 (1997).
4) Seo S.-Y., Sharma V. K., Sharma N., *J. Agric. Food Chem.*, **51**, 2837—2853 (2003).
5) Dai Y., Zhou G. X., Kurihara H., Ye W. C., Yao X. S., *J. Nat. Prod.*, **69**, 1022—1024 (2006).
6) Hara S., Okabe H., Mihashi K., *Chem. Pharm. Bull.*, **35**, 501—507 (1987).
7) Kubo I., Kinst-Hori I., *J. Agric. Food Chem.*, **47**, 4121—4125 (1999).
8) Kubo I., Kinst-Hori I., Chaudhuri S. K., Kubo Y., Sanchez Y., Ogura T., *Bioorg. Med. Chem.*, **8**, 1749—1755 (2000).
9) Mason H. S., Peterson E. W., *Biochim. Biophys. Acta*, **111**, 134—146 (1965).