New Flavanol Glucosides from *Abacopteris aspera* (PRESL) CHING

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Three new flavanol glycosides, **1**–**3**, and eight known compounds, **4**–**11**, were isolated from a MeOH extract of the fern *Abacopteris aspera* (PRESL) CHING. Their structures were elucidated on the basis of extensive spectroscopic analysis, including HSQC, HMBC, ^{1}H,^{1}H-COSY, and NOESY experiments, acid hydrolysis, and by the comparison of their NMR data with those of related compounds.

Introduction. – The fern *Abacopteris aspera* (PRESL) CHING (Thelypteridaceae family) is widely distributed in the south of China and other tropical regions [1]. The plant has been used in Chinese medicine to relieve redness, heat, and swelling of sore throat caused by acute and chronic pharyngitis [2][3]. Previous phytochemical investigations on the genus *Abacopteris* revealed the occurrence of rare flavan-4-ols, 3-deoxyanthocyanins, and *C*-methylflavonoids [4–16], among which flavan-4-ols are considered as the main characteristic constituents. Recently, several pharmacological features of flavan-4-ols have been studied, which include cytotoxic, anti-inflammation, hypolipidemic potential, and vascular protective activities [10][17–19]. There are no previous reports on the constituents and biological properties of this medicinal plant. A phytochemical investigation of the whole plants of *A. aspera* was thus performed as a part of our continuous search for new or bioactive compounds from *Abacopteris* species. Herein, we report the isolation and structure elucidation of three new flavanol glycosides, **1**–**3**, and eight known compounds, **4**–**11** (*Fig. 1*) from *A. aspera*.

Results and Discussion. – Air-dried whole plants of *A. aspera* were extracted with MeOH to give a residue, which was suspended in H_2O and extracted sequentially with petroleum ether (PE), AcOEt, and BuOH. The BuOH and AcOEt extracts were then subjected to column chromatography on silica gel, octadecyl silica (ODS), *Sephadex LH-20*, and macroporous resin, and to semi-preparative HPLC, to afford eleven compounds, **1**–**11**. The structures of the new compounds **1**–**3** were determined by extensive spectroscopic analyses, including HSQC, HMBC, ^{1}H,^{1}H-COSY, and NOESY techniques, and acid hydrolysis.

[1]) These authors contributed equally to this work.

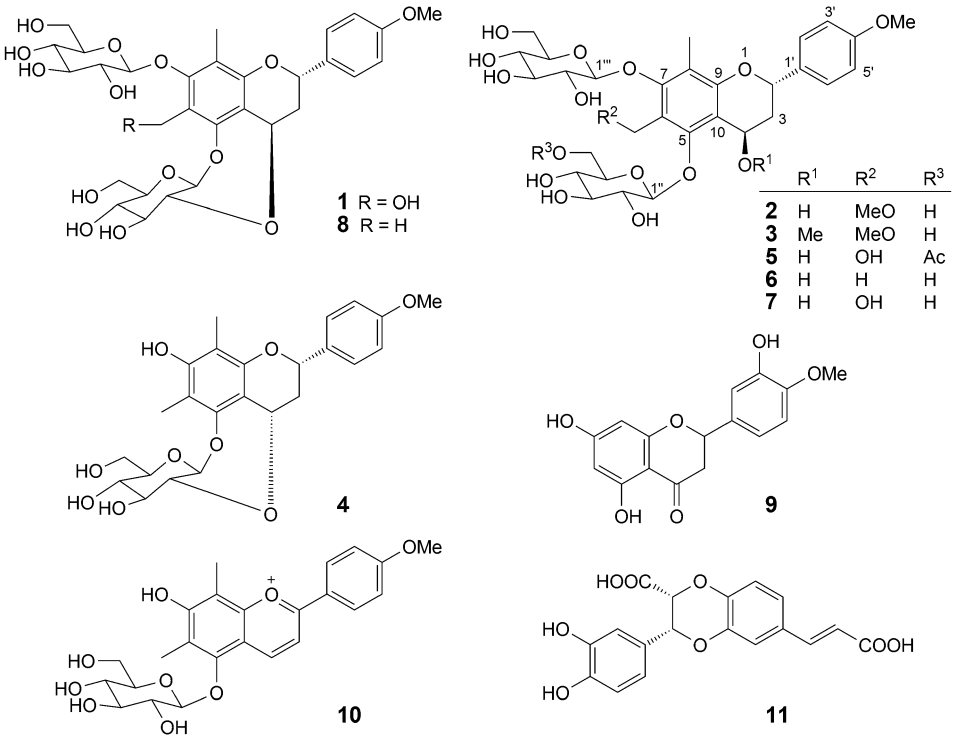

Fig. 1. *Structures of compounds* **1**–**11**

Compound **1**, white amorphous powder, had the molecular formula $C_{30}H_{38}O_{15}$ as deduced from its ^{13}C-NMR and HR-ESI-TOF-MS data (*m/z* 661.2070 ($[M+Na]^+$)). The IR spectrum showed absorptions due to OH (3421 cm^{-1}) and phenyl (1614, 1519 cm^{-1}) groups. The ^{1}H-NMR spectrum showed characteristic signals of a Me group (δ(H) 2.70 (*s*)), a MeO group (δ(H) 3.71 (*s*)), two anomeric H-atoms (δ(H) 5.62 (*d*, *J* = 8.4, 1 H) and 5.49 (*d*, *J* = 7.2, 1 H)), and four aromatic H-atoms (as two *doublet*s at δ(H) 7.36 (*d*, *J* = 8.8, 2 H) and 7.01 (*d*, *J* = 8.8, 2 H)), suggesting a *para*-substituted phenyl group (*Table*). The ^{13}C-NMR data of **1** analyzed with the aid of the DEPT and HSQC spectra revealed the presence of two Me, four sp^3 CH_2, four sp^2 CH, and twelve sp^3 CH groups, and eight sp^2 quaternary C-atoms (*Table*). The ^{1}H- and ^{13}C-NMR signals (*Table*) of **1** were completely assigned by a combination of HSQC, HMBC, and ^{1}H,^{1}H-COSY experiments (*Fig. 2*). According to the ^{1}H,^{1}H-COSY and HSQC spectra, the substructure, –CH–CH_2–CH– was deduced from the correlation CH_2(3) (δ(H) 2.33 and 2.05)/H–C(2) (δ(H) 4.99) and H–C(4) (δ(H) 5.21) (*Fig. 2*). In the HMBC spectrum, correlations (*Fig. 2*) H–C(4)/C(5) (δ(C) 151.9), C(9) (δ(C) 154.7), and C(10) (δ(C) 109.8); CH_2(11) (δ(H) 5.51 and 5.18)/C(5), C(6) (δ(C) 121.7), and C(7) (δ(C) 156.3); and Me–C(8) (δ(H) 2.70)/C(7), C(8) (δ(C) 117.2), and C(9) indicated the presence of a 5,7-disubstituted 6-methylene-8-methylchromane ring. Additionally, correlations H–C(2) (δ(H) 4.99)/C(1′) (δ(C) 133.6) and C(2′,6′) (δ(C) 128.7);

Table. *^{1}H- and ^{13}C-NMR Data* (400 and 100 MHz; (D_5)pyridine) *of* **1**–**3**. δ in ppm, J in Hz.

Position	**1**		**2**		**3**	
	δ(H)	δ(C)	δ(H)	δ(C)	δ(H)	δ(C)
2	4.99 (br. *d*, *J* = 11.6)	74.7	5.75 (br. *d*, *J* = 11.6)	73.8	5.59 (*dd*, *J* = 2.4, 12.0)	73.7
3	2.33 (br. *d*, *J* = 14.4), 2.05 (*ddd*, *J* = 3.2, 11.6, 14.4)	37.5	2.42 (br. *d*, *J* = 13.6), 1.90 (*ddd*, *J* = 3.2, 11.6, 13.6)	38.3	2.42 (*dt*, *J* = 2.4, 14.0), 1.88 (*ddd*, *J* = 2.4, 12.0, 14.0)	34.9
4	5.21 (*d*, *J* = 3.2)	66.2	5.53 (*d*, *J* = 3.2)	58.8	5.70 (*t*, *J* = 2.4)	67.9
5		151.9		155.0		156.1
6		121.7		118.1		118.4
7		156.3		157.5		157.6
8		117.2		117.4		116.9
9		154.7		155.1		155.6
10		109.8		117.4		112.9
11	5.51 (br. *d*, *J* = 11.2), 5.18 (br. *d*, *J* = 11.2)	55.3	5.48 (*d*, *J* = 9.2), 5.44 (*d*, *J* = 9.2)	65.2	5.37 (*d*, *J* = 9.6), 5.31 (*d*, *J* = 9.6)	66.7
*Me*O–C(4)					3.69 (*s*)	56.5
Me–C(8)	2.70 (*s*)	10.5	2.65 (*s*)	11.1	2.60 (*s*)	11.1
*Me*O–C(11)			3.69 (*s*)	58.1	3.66 (*s*)	58.7
1′		133.6		135.1		134.9
2′,6′	7.36 (*d*, *J* = 8.8)	128.7	7.50 (*d*, *J* = 8.8)	128.5	7.45 (*d*, *J* = 8.8)	128.5
3′,5	7.01 (*d*, *J* = 8.8)	114.8	7.04 (*d*, *J* = 8.8)	114.9	7.04 (*d*, *J* = 8.8)	114.9
4′		160.5		160.3		160.4
*Me*O–C(4′)	3.71 (*s*)	55.8	3.70 (*s*)	55.7	3.71 (*s*)	55.7
5-*O*-Glc						
1″	5.62 (*d*, *J* = 8.4)	101.6	5.94 (*d*, *J* = 6.8)	106.9	5.67 (*d*, *J* = 7.6)	107.8
2″	3.90–3.93 (*m*)	79.0	4.35–4.38 (*m*)	76.1	4.37–4.40 (*m*)	76.9
3″	4.29–4.32 (*m*)	76.6	4.28–4.30 (*m*)	79.1	4.30–4.32 (*m*)	79.4
4″	4.18 (*t*, *J* = 9.2)	72.6	4.33–4.36 (*m*)	71.9	4.33–4.36 (*m*)	72.3
5″	3.91–3.94 (m)	76.4	4.02–4.05 (*m*)	79.4	4.07–4.11 (*m*)	79.1
6″	4.45 (*dd*, *J* = 2.8, 12.0), 4.25–4.28(*m*)	63.7	4.45 (*dd*, *J* = 2.4, 8.8), 4.37–4.39(*m*)	62.5	4.38–4.41 (*m*), 4.30–4.33 (*m*)	63.3
7-*O*-Glc						
1‴	5.49 (*d*, *J* = 7.2)	106.6	5.54 (*d*, *J* = 7.2)	107.1	5.66 (*d*, *J* = 7.2)	106.9
2‴	4.38–4.40 (*m*)	76.4	4.32–4.35 (*m*)	76.5	4.32–4.35 (*m*)	76.4
3‴	4.30–4.33 (*m*)	78.8	4.34–4.37 (*m*)	78.8	4.33–4.35 (*m*)	78.7
4‴	4.06–4.08 (*m*)	71.5	4.28–4.30 (*m*)	72.4	4.24 (*t*, *J* = 9.2)	72.5
5‴	4.07–4.10 (*m*)	80.1	3.93–3.96 (*m*)	78.9	3.86–3.89 (*m*)	78.8
6‴	4.51 (br. *d*, *J* = 11.2), 4.33–4.36 (*m*)	62.8	4.46 (*dd*, *J* = 2.4, 11.2), 4.29–4.32 (*m*)	63.6	4.58 (*dd*, *J* = 2.4, 11.2), 4.33–4.36 (*m*)	63.8

H–C(2′,6′)/C(2) (δ(C) 74.7) revealed that the *para*-substituted phenyl group was attached to C(2) of the chromane ring. From these data and by comparison with the spectra of flavan-4-ol-type glycosides previously isolated from *Abacopteris* plants [7–9], compound **1** could be assigned as a flavan-4-ol-type glycoside with two sugar units. Analysis of the NMR data of the sugar units (*Table*) suggested that the two sugars

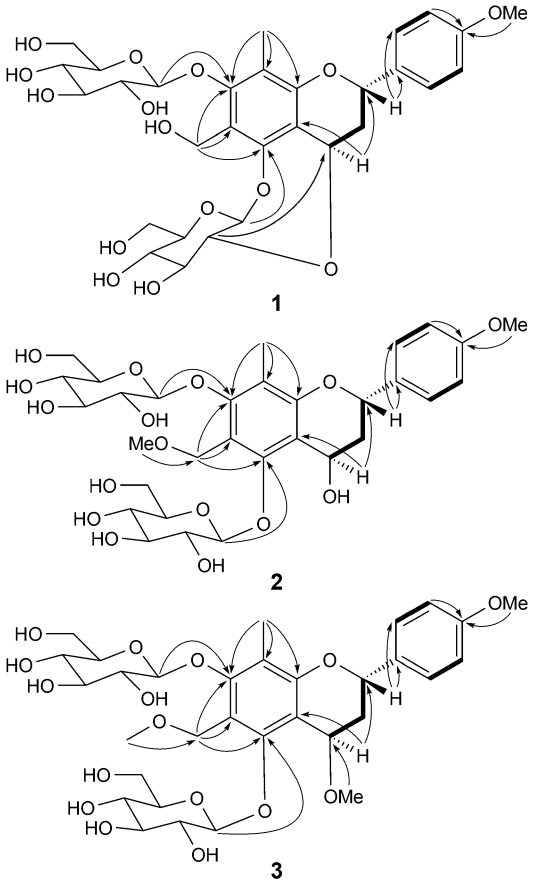

Fig. 2. *Key HMBCs* (H → C) *and* $^1H,^1H$*-COSY* (—) *correlations of compounds* **1**–**3**

were both β-D-glucoses, which was confirmed by acid hydrolysis and GC analysis of the thiazolidine derivative.

As observed in the HMBC spectrum (*Fig. 2*), the anomeric H–C(1″) (δ(H) 5.62) correlated with C(5) (δ(C) 151.9), and H–C(1‴) (δ(H) 5.49) with C(7) (δ(C) 156.3), indicating that two β-D-glucoses were connected with C(5) and C(7), respectively. In addition, correlations H–C(2″) (δ(H) 3.90–3.93)/C(4) (δ(C) 66.2), and H–C(4) (δ(H) 5.21)/C(2″) (δ(C) 79.0) evidenced that C(2″) was linked to C(4) through a O-bridge. The position of the MeO group at C(4′) was deduced from the HMBC δ(H) 3.71 (MeO–C(4′))/δ(C) 160.5 (C(4′)). Comparison of the above NMR spectroscopic data of **1** with those of the co-occurring compound **8** (abacopterin I [9]) disclosed that **1** had a very similar structure, except for the disappearance of a Me group and the appearance of a new O-bearing CH_2 group resonating at δ(C) 55.3 (CH_2(11)). The presence of the CH_2(6)–O group was confirmed by the HMBC CH_2(11)/C(5), C(6), and C(7).

To establish the configurations at C(2) and C(4), the chemical shifts and coupling constants of H–C(2), CH_2(3), and H–C(4), and CD spectrum were examined in detail. The coupling constants of H–C(2) (br. *d*, $J = 11.6$) and H–C(4) (*d*, $J = 3.2$) suggested that H–C(2) and H–C(4) were *trans*-configurated [9], and this was supported by the NOESY spectrum, in which no cross-peak H–C(2)/H–C(4) was observed. In the CD spectrum, a positive *Cotton* effect at 283 nm was observed, which was very close to that of abacopterin I (**8**) [9], indicating (4*R*)-configuration at C(4). On the basis of these evidences, the absolute configurations at C(2) and C(4) were established as (2*S*) and (4*R*). Thus, the structure of **1** was finally elucidated as 1,2-*O*-[(2*S*,4*R*)-7-(*β*-D-glucopyranosyloxy)-3,4-dihydro-6-(hydroxymethyl)-2-(4-methoxyphenyl)-8-methyl-2*H*-1-benzopyran-5,4-diyl] *β*-D-glucopyranose.

Compound **2** was obtained as white needles (MeOH), and its molecular formula, $C_{31}H_{42}O_{16}$, was deduced from its HR-ESI-TOF-MS (*m*/*z* 693.2358 ($[M + Na]^+$; calc. 693.2371)) and ^{13}C-NMR spectra. The IR spectrum displayed absorption bands for OH (3423 cm^{-1}) and phenyl (1601, 1516 cm^{-1}) groups. The ^{1}H-NMR spectrum of **2** exhibited a pair of A_2B_2-type signals (δ(H) 7.50, 7.04 (2*d*, $J = 8.8$, 2 H each), attributed to a *para*-substituted phenyl group, and signals of one Me group (δ(H) 2.65 (*s*)), two MeO groups (δ(H) 3.70 (*s*) and δ(H) 3.69 (*s*)), and two anomeric H-atoms (δ(H) 5.94 (*d*, $J = 6.8$, 1 H) and 5.54 (*d*, $J = 7.2$, 1 H)), suggesting two sugar moieties (*Table*). The ^{13}C-NMR spectrum (*Table*) analyzed with the aid of the DEPT and HSQC spectra further supported these results. On acid hydrolysis of **2**, only D-glucose was detected by GC. The *β*-pyranosyl configuration of the glycosidic bonds was deduced from the coupling constants of the anomeric H-atoms and the ^{13}C-NMR data of the sugars (*Table*). From the above mentioned evidence, in conjunction with biogenetic considerations, **2** was considered to be a flavan-4-ol-type glycoside.

The ^{1}H- and ^{13}C-NMR data of **2** were very similar to those of triphyllin A [5], except for the appearance of a MeO signal in the spectra of **2**. This was confirmed by analyses of the 2D-NMR data of **2**. The HMBCs (*Fig. 2*) CH_2(11) (δ(H) 5.48 and 5.44)/C(6) (δ(C) 118.1), and MeO–C(11) (δ(H) 3.69)/C(11) (δ(C) 65.2) suggested that a MeO-carrying CH_2 group was attached to C(6). Two *β*-D-glucoses were attached to C(5) and C(7) respectively, and the position of the Me group was determined to be at C(8), as judged by the HMBCs H–C(1″) (δ(H) 5.94)/C(5) (δ(C) 155.0); H–C(1‴) (δ(H) 5.54)/C(7) (δ(C) 157.5); and Me–C(8) (δ(H) 2.65)/C(8) (δ(C) 117.4).

In the CD spectrum of **2**, a negative *Cotton* effect at 225 nm, and positive *Cotton* effects at 238 and 280 nm were observed, which were quite comparable to those of triphyllin A [8]. The signals of H–C(2) (br. *d*, $J = 11.6$), CH_2(3) (br. *d*, $J = 13.6$; *ddd*, $J = 3.2, 11.6, 13.6$), and H–C(4) (*d*, $J = 3.2$) were also consistent with those of triphyllin A. These evidences implied that **2** had the same configuration (2*S*,4*R*) as triphyllin A. Therefore, the structure of **2** was deduced to be (2*S*,4*R*)-5-(*β*-D-glucopyranosyloxy)-3,4-dihydro-4-hydroxy-6-(methoxymethyl)-2-(4-methoxyphenyl)-8-methyl-2*H*-1-benzopyran-7-yl *β*-D-Glucopyranoside.

Compound **3** was obtained as white amorphous powder (MeOH) with the molecular formula of $C_{32}H_{44}O_{16}$ as deduced from its HR-ESI-TOF-MS (*m*/*z* 707.2532 ($[M + Na]^+$; calc. 707.2527)) and ^{13}C-NMR data. The IR spectrum indicated the presence of OH (3405 cm^{-1}), and phenyl (1599, 1516 cm^{-1}) groups. The ^{1}H- and ^{13}C-NMR data of **3** (*Table*) were very similar to those of **2**, evidencing the presence of a

MeO group instead of a OH group at C(4). The HMBC (*Fig. 2*) MeO–C(4) (δ(H) 3.69)/C(4) (δ(C) 67.9) indicated that the MeO group was located at C(4). The configurations at C(2) and C(4) were determined as (2*S*) and (4*R*) by comparing the coupling constants of key H-atoms, and, CD and NOESY data of **3** with those of **2**. Thus, **3** was identified as (2*S*,4*R*)-5-(β-D-glucopyranosyloxy)-3,4-dihydro-4-methoxy-6-(methoxymethyl)-2-(4-methoxyphenyl)-8-methyl-2*H*-1-benzopyran-7-yl β-D-glucopyranoside.

The known compounds abacopterin C (**4**) [8], 6″-*O*-acteyltriphyllin A (**5**) [12], eruberin B (**6**) [5], triphyllin A (**7**) [5], abacopterin I (**8**) [9], hesperitin (**9**) [20], 7-hydroxy-4′-methoxy-6,8-dimethylanthocyanidin 5-*O*-β-D-glucopyranoside (**10**) [4] [15], and *rel*-(2*R*,3*R*)-6-(2-carboxyethenyl)-3-(3,4-dihydroxyphenyl)-2-carboxy-1,4-benzodioxin (caffeicin B; **11**) [13][14] were identified by comparison of their spectroscopic data with those reported in the literature. Compound **9** was found for the first time from the genus *Abacopteris*.

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Experimental Part

General. TLC: Silica gel GF_{254} pre-coated plates (*Qindao Marine Chemical Co., Ltd.*). Column chromatography (CC): silica gel (SiO_2, 100–200, 200–300, 300–400 mesh; *Qindao Marine Chemical Co., Ltd.*), *Sephadex LH-20* (25–100 μm; *Fluka BioChemika*), CHP resin (*Mitsubishi Chemical Holdings*), and ODS gel (230–400 mesh; *Fluka BioChemika*). Semi-prep. HPLC: *CE2000* liquid chromatograph with a UV detector (*DaLian Elite Analytical Instruments Co., Ltd.*) and a *Kromasil 100-5* C_{18} column (250 mm × 4.6 mm, 5 μm). GC: *Shimadzu GC-2010 plus* gas chromatograph; cap. column (30 m × 0.25 mm × 0.25 μm, *RTX-WAX*); detection, FID; temp. for injector, 230°, and for detector, 250°; N_2 as carrier gas; temp. for the oven, 220°. M.p.: *X4* micro-melting-point apparatus. Optical rotations: *Autopol IV* automatic polarimeter. Circular dichroism (CD) and UV spectra: *Chirascan* spectropolarimeter; λ_{max} (log ε) in nm. IR Spectra: *Nicolet Nexus 300* FT-IR spectrometer; KBr disk; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Bruker DRX-400 AV400* instrument; at 400 (^{1}H) and 100 MHz (^{13}C); (D_5)pyridine, $CDCl_3$, or (D_6)DMSO as solvent; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. HR-ESI-TOF-MS: *Acquity UPLC-Q-Tof Micro MS* spectrometer; in *m*/*z*.

Plant Material. Whole plants of *A. aspera* were collected in Ruyuan County, Guangdong Province of China in January 2009, and identified by *C. Z.* (Institute of Clinical Pharmacology, Guangzhou University of Chinese Medicine). A voucher specimen (XYJ2009-01) has been deposited with School of Chinese Materia Medica, Guangzhou University of Chinese Medicine.

Extraction and Isolation. The air-dried whole plants of *A. aspera* (1.05 kg) were pulverized and extracted with MeOH (2 l × 5) at r.t. for a week. The MeOH extract was concentrated under reduced pressure to leave a residue (150 g), which was suspended in H_2O (700 ml) and then partitioned with petroleum ether (PE; 3 × 700 ml), AcOEt (3 × 700 ml), and BuOH (5 × 700 ml) sequentially. The BuOH extract (80 g) was subjected to CC (CHP resin; MeOH/H_2O 30:70 → 95:5) to give *Frs. A1–A6*. *Fr. A1* (4.5 g) was dissolved under heating in 60% aq. MeOH and allowed to reach saturation, and then crystallized at r.t. to give **7** (3.2 g). *Fr. A2* (5.0 g) was separated by CC (ODS; MeOH/H_2O 35:65 → 50:50) to afford six subfractions, *Frs. A2.1–A2.6*, and *Fr. A3* (4.1 g) was subjected to CC (*Sephadex LH-20*; MeOH/H_2O 60:40 → 75:25) to yield four subfractions *Frs. A3.1–A3.4*. *Fr. A2.4* (1.5 g) was purified by CC (SiO_2; $CHCl_3$/MeOH/H_2O 6:1:0.1) to yield **8** (947 mg). *Fr. A3.2* (2.5 g) was separated by CC (ODS; MeOH/H_2O 30:70 → 60:40) to give eight subfractions, *Frs. A3.2.1–A3.2.8*, then *Fr. A3.2.2* (0.2 g) was further purified by CC (SiO_2; $CHCl_3$/MeOH/H_2O 5:1:0.1) to yield **2** (36 mg), and *Fr. A3.2.5* (1.6 g) was further purified by recrystallization from MeOH/H_2O 90:10 to give **5** (46 mg). *Frs. A3.2.6* and

A2.2 were combined (1.3 g) and purified by CC (SiO_2; $CHCl_3$/MeOH/H_2O 5:1:0.1) to yield **6** (382 mg), and its subfractions mainly containing **3** was further purified by repeated semi-prep. HPLC (*Kromasil 100-5 C_{18}*; MeOH/H_2O 1:1) to afford **3** (130 mg). *Frs. A3.2.8* and *A2.6* were combined (0.4 g) and dissolved in MeOH. A red solid precipitated during evaporation of the solvent at r.t., which was filtered to yield **10** (23 mg), and the filtrate was further separated by CC (SiO_2; $CHCl_3$/MeOH/H_2O 7:1:0.05 → 5:1:0.1) to furnish **1** (57 mg).

The AcOEt extract (20 g) was subjected to CC (SiO_2; $CHCl_3$/MeOH 50:1 → 2:1) to give *Frs. B1 – B13*. *Fr. B1* (1.2 g) was separated by CC (*Sephadex LH-20*; $CHCl_3$/MeOH 1:1), followed by a further CC (SiO_2; PE/acetone 2:1) to yield **9** (148 mg). *Fr. B6* (1.1 g) was purified by CC (*Sephadex LH-20*; $CHCl_3$/MeOH 1:1) to afford **4** (26 mg). *Fr. B8* (0.5 g) was subjected to CC (*Sephadex LH-20*; $CHCl_3$/MeOH 1:1), followed by a further CC (ODS; MeOH/H_2O/HCOOH 4:6:0.1), and finally purified by CC (*Sephadex LH-20*; MeOH) to yield **11** (140 mg).

Acidic Hydrolysis. Each compound (2 mg) was hydrolyzed with 9% HCl (2 ml) at 90° for 5 h. After cooling, the mixture was filtered, and then the filtrate was dried under vacuum at low temp. The residues were converted to thiazolidine derivatives for GC analysis as described in [8].

1,2-O-*[(2*S*,4*R*)-7-(β*-D-*Glucopyranosyloxy)-3,4-dihydro-6-(hydroxymethyl)-2-(4-methoxyphenyl)-8-methyl-2*H*-1-benzopyran-5,4-diyl] β*-D-*Glucopyranose*; **1**). White amorphous powder (MeOH). $[\alpha]_D^{15} = +69$ ($c = 0.145$, MeOH). CD (MeOH): 225 (−0.47), 236 (+0.12), 283 (+0.42). UV (MeOH): 210 (3.99), 226 (3.63), 274 (2.59), 281 (2.59). IR (KBr): 3421, 2918, 1614, 1519, 1459, 1384, 1245, 1153, 1072, 806. ^{1}H- and ^{13}C-NMR: see the *Table*. HR-ESI-TOF-MS: 661.2070 ($[M+Na]^+$, $C_{30}H_{38}NaO_{15}^+$; calc. 661.2108).

*(2*S*,4*R*)-5-(β*-D-*Glucopyranosyloxy)-3,4-dihydro-4-hydroxy-6-(methoxymethyl)-2-(4-methoxyphenyl)-8-methyl-2*H*-1-benzopyran-7-yl β*-D-*Glucopyranoside* (**2**). White needles (MeOH). M.p. 177–180°. $[\alpha]_D^{15} = +20$ ($c = 0.193$, MeOH). CD (MeOH): 225 (−1.30), 238 (+0.27), 280 (+0.29). UV (MeOH): 209 (4.16), 215 (3.92), 227 (3.71), 274 (2.67), 281 (2.63). IR (KBr): 3423, 2925, 1601, 1516, 1458, 1385, 1249, 1158, 1076, 838. ^{1}H- and ^{13}C-NMR: see the *Table*. HR-ESI-TOF-MS: 693.2358 ($[M+Na]^+$, $C_{31}H_{42}NaO_{16}^+$; calc. 693.2371).

*(2*S*,4*R*)-5-(β*-D-*Glucopyranosyloxy)-3,4-dihydro-4-methoxy-6-(methoxymethyl)-2-(4-methoxyphenyl)-8-methyl-2*H*-1-benzopyran-7-yl β*-D-*Glucopyranoside* (**3**). White amorphous powder (MeOH). $[\alpha]_D^{15} = -11$ ($c = 0.200$, MeOH). CD (MeOH): 214 (−2.43), 238 (+1.81), 279 (+0.23). UV (MeOH): 210 (4.18), 226 (3.75), 275 (2.75), 281 (2.73). IR (KBr): 3405, 2926, 1599, 1516, 1456, 1385, 1250, 1154, 1073, 833. ^{1}H- and ^{13}C-NMR: see the *Table*. HR-ESI-TOF-MS: 707.2532 ($[M+Na]^+$, $C_{32}H_{44}NaO_{16}^+$; calc. 707.2527).

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