Iridoid Glycosides from *Gardenia jasminoides* ELLIS

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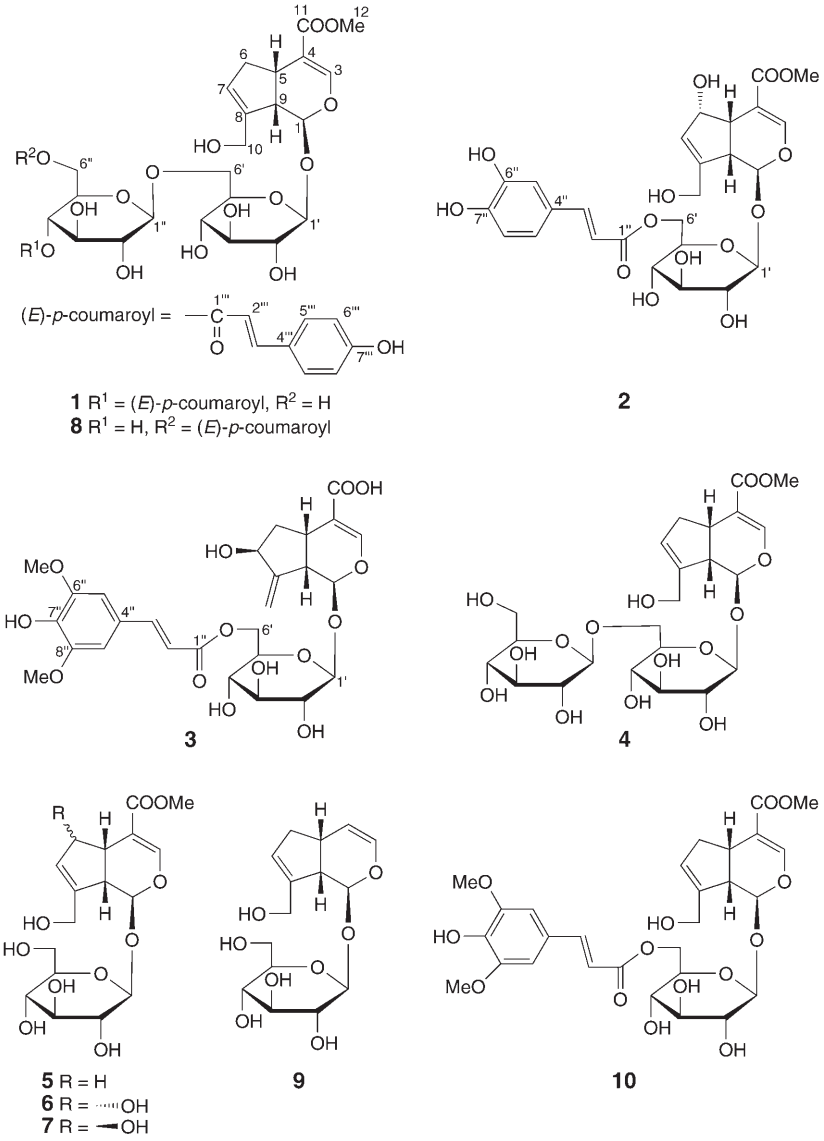
Three new iridoid glycosides, 4″-*O*-[(*E*)-*p*-coumaroyl]gentiobiosylgenipin (**1**), 6′-*O*-[(*E*)-caffeoyl]-deacetylasperulosidic acid methyl ester (**2**), and 6′-*O*-[(*E*)-sinapoyl]gardoside (**3**), together with seven analogues, **4**–**10**, were isolated from the BuOH extract of the fruits of *Gardenia jasminoides* ELLIS. Their structures were determined by means of spectroscopic analyses, including HR-ESI-MS, IR, and ^{1}H- and ^{13}C-NMR, and 2D experiments (COSY, HSQC, and HMBC), and comparison with known related compounds.

Introduction. – The genus of *Gardenia* (family Rubiaceae) consists of more than 250 species spread among many countries of the world. The *Gardenia* plants are used in folk medicine for their contraceptive, febrifuge, analgesic, diuretic, larvicide, hypotensive, antibacterial activities, as well as anxiolytic and antiplasmodial effects, and for the treatment of headaches [1–6]. The chemical constituents of the *Gardenia* plants are reported to be triterpenes [7], flavonoids [8], iridoid glycosides [9], quinic acid derivatives [10], amides [11], and fatty acids. *Gardenia jasminoides* ELLIS is an evergreen shrub, widely spread in the southern area of China, growing on mountain slop or on road sides as a decorative plant. The fruit of this plant is recorded as *Fructus Gardeniae* ('*Zhizi*') in Chinese Pharmacopoeia [12] and shows diuretic, cholagogue, anti-inflammatory, and antihyperlipidemic effects [13–15]. The principle bioactive components reported from *Gardenia jasminoides* fruit are iridoid glycosides, *e.g.*, geniposide, genipin gentiobioside, gardenoside, scandoside methyl ester; shanzhiside, 10-acetylgeniposide, deacetylasperulosidic acid methyl ester *etc.*, which indicated cholagogue, anti-inflammatory, analgesia, antifungal, and anti-cancer effects [16][17]. This paper deals with the isolation and structural elucidation of three new iridoid glycosides, **1**–**3**, along with seven known analogues, **4**–**10**, from the fruit of *Gardenia jasminoides*.

Results and Discussion. – The air-dried and powdered fruits were extracted with 80% EtOH to give the crude extract (*ca.* 3 kg). The total extract was suspended in H_2O and successively partitioned with petroleum ether, AcOEt, and BuOH. The BuOH



fraction was separated by column chromatography over MCI gel, silica gel, and *Sephadex LH-20* repeatedly, followed by semi-preparative HPLC, and afforded a series of iridoid glycosides, including three new compounds, **1**–**3**, and seven known ones, **4**–**10**. The structures of the known compounds were confirmed by comparison of their physical and spectral data with the published data, as genipin gentiobioside (**4**), geniposide (**5**), deacetylasperulosidic acid methyl ester (**6**), scandoside methyl ester (**7**), 6″-*O*-[(*E*)-*p*-coumaroyl]genipin gentiobioside (**8**), bartsioside (**9**), 6′-*O*-sinapoyl-geniposide (**10**) [18].

Compound **1**, a pale yellow powder, has a molecular formula of $C_{32}H_{40}O_{17}$ on the basis of its positive-ion HR-ESI-MS (*m/z* 719.21683 ($C_{32}H_{40}NaO_{17}^{+}$; calc. 719.21577). The molecular formula of **1** was the same as that of 6″-*O*-[(*E*)-*p*-coumaroyl]genipin gentiobioside (**8**), moreover, the NMR data were very similar. The IR spectrum revealed the absorption bands of OH (3411 cm^{-1}) and C=O (1697 cm^{-1}) groups. The ^{1}H- and ^{13}C-NMR spectral data of **1** (*Table 1*) showed signals of a coumaroyl group (δ(H) 6.64 (*d*, *J* = 15.8, 1 H), 8.02 (*d*, *J* = 15.8, 1 H), 7.61 (*d*, *J* = 8.0, 2 H), 7.24 (*d*, *J* = 8.0, 2 H); δ(C) 167.3, 115.2, 145.8, 126.2, 130.9, 116.9, 161.6). The resonances at δ(H) 5.39 (*d*, *J* = 7.9, H−C(1′)) and 5.27 (*d*, *J* = 7.8, H−C(1″)) were attributed to the two anomeric H-atoms of the hexose units. The corresponding ^{13}C-NMR resonances were observed at δ(C) 101.2 and 105.2, respectively. The chemical shifts and coupling constants of the sugar signals indicated the presence of β-gentiobioside. Furthermore, the signals at δ(H) 5.87 (*d*, *J* = 7.4, H−C(1)), 7.75 (br. *s*, H−C(3)), 6.31 (br. *s*, H−C(7)), 4.95 (*d*, *J* = 14.8, H_a−C(10)), 4.70 (*d*, *J* = 14.8, H_b−C(10)), and 3.68

Table 1. *^{1}H- and ^{13}C-NMR Data of* **1** *at 500 and 125 MHz, Respectively, in(D_5)Pyridine.* Chemical shifts δ in ppm, *J* in Hz.

	δ(H)	δ(C)
H−C(1)	5.87 (*d*, *J* = 7.4)	98.3 (*d*)
H−C(3)	7.75 (*s*)	152.5 (*d*)
C(4)	–	111.7 (*s*)
H−C(5)	3.45–3.40 (*m*)	35.9 (*d*)
CH_2(6)	3.05 (*dd*, *J* = 16.8, 8.2), 2.61 (br. *d*, *J* = 16.8)	39.3 (*d*)
H−C(7)	6.31 (*s*)	127.3 (*d*)
C(8)	–	145.6 (*s*)
H−C(9)	3.11 (*dd*, *J* = 7.5, 7.5)	47.0 (*d*)
CH_2(10)	4.95 (*d*, *J* = 14.8), 4.77 (*d*, *J* = 14.8)	61.0 (*t*)
C(11)	–	167.8 (*s*)
Me(12)	3.68 (*s*)	51.1 (*q*)
H−C(1′)	5.39 (*d*, *J* = 7.9)	101.2 (*d*)
H−C(2′)	4.25–4.27 (*m*)	78.4 (*d*)
H−C(3′)	4.08–4.11 (*m*)	74.8 (*d*)
H−C(4′)	4.23–4.25 (*m*)	78.3 (*d*)
H−C(5′)	3.95–3.99 (*m*)	71.8 (*d*)
CH_2(6′)	4.85 (*dd*, *J* = 11.0, 1.9), 4.32 (*dd*, *J* = 11.0, 6.0)	70.0 (*t*)
H−C(1″)	5.27 (*d*, *J* = 7.8)	105.2 (*d*)
H−C(2″)	4.14–4.17 (*m*)	75.6 (*d*)
H−C(3″)	4.47–4.51 (*m*)	75.9 (*d*)
H−C(4″)	5.84 (*dd*, *J* = 9.4, 9.4)	72.9 (*d*)
H−C(5″)	4.24–4.25 (*m*)	76.4 (*d*)
CH_2(6″)	4.32 (*dd*, *J* = 12.4, 4.9), 4.27 (*dd*, *J* = 11.3, 2.0)	62.4 (*t*)
C(1‴)	–	167.3 (*s*)
H−C(2‴)	6.64 (*d*, *J* = 15.8)	115.2 (*d*)
H−C(3‴)	8.02 (*d*, *J* = 15.8)	145.8 (*d*)
C(4‴)	–	126.2 (*s*)
H−C(5‴,9‴)	7.61 (*dd*, *J* = 8.6, 1.3)	130.9 (*d*)
H−C(6‴,8‴)	7.24 (*dd*, *J* = 8.6, 1.3)	116.9 (*d*)
C(7‴)	–	161.6 (*s*)

(COOMe), as well as the ^{13}C signals at δ(C) 98.3 (C(1)), 152.5 (C(3)), 111.7 (C(4)), 127.3 (C(7)), 145.6 (C(8)), 61.0 (C(10)), 167.8 (C(11)), and 51.1 (C(12)) were attributed to the iridoid skeleton of genipin.

Interpretation of the ^{1}H,^{1}H-COSY, HMQC, and HMBC spectra of **1** (*Fig. 1*) revealed the substitution pattern, and allowed us to fully assign all ^{1}H- and ^{13}C-NMR signals. The coumaroyl group was located at C(4″), as corroborated by HMBC correlations of H–C(4″)/C(1‴). The attachment of the β-D-gentiobioside moiety at C(1) was established by HMBC correlations of H–C(1′)/C(1) and H–C(1)/C(1′). The presence of a COOMe group was confirmed by HMBC correlation of Me–C(12)/C(11). From these data, the structure of **1** was elucidated as 4″-*O*-[(*E*)-*p*-coumaroyl]gentiobiosylgenipin[1]), a new acylated iridoid glycoside.

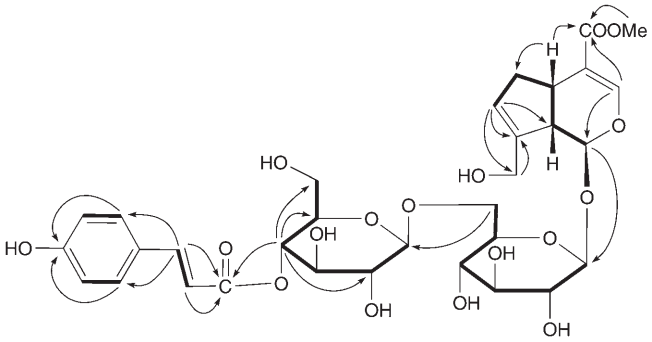


Fig. 1. *Selected HMBC* (H → C) *and* ^{1}*H,*^{1}*H-COSY* (—) *correlations of* **1**

Compound **2**, a pale yellow powder, has a molecular formula of $C_{26}H_{30}O_{14}$ based on its positive-ion HR-ESI-MS (*m*/*z* 589.15350 ($C_{26}H_{30}NaO_{14}^+$; calc. 589.15278). The IR spectrum revealed the absorption bands of OH (3426 cm^{-1}) and C=O (1693 cm^{-1}) groups. The signals at δ(H) 6.21 (*d*, *J* = 15.8, 1 H), 7.49 (*d*, *J* = 15.8, 1 H) and δ(C) 169.1, 115.1, 147.6, and signals of an extra set of *ABX*-type aromatic H-atoms at δ(H) 6.70 (*d*, *J* = 8.2, 1 H), 6.87 (*dd*, *J* = 8.2, 1.3, 1 H), 6.96 (*d*, *J* = 1.3, 1 H) indicated the presence of a caffeoyl group. The anomeric signal at δ(H) 4.64 (*d*, *J* = 7.8 Hz, 1 H) and the signals in the region δ(H) 3.16–3.77, together with the relevant ^{13}C-NMR resonances (*Table 2*), indicated the presence of a β-glucopyranose (Glc) unit. The signals at δ(H) 5.00 (*d*, *J* = 8.9, H–C(1)), 7.55 (br. *s*, H–C(3)), 4.70 (*d*, *J* = 15.6, H–C(6)), 5.95 (br. *s*, H–C(7)), 4.99 (*dd*, *J* = 9.0, 4.4, H_a–C(10)), 4.77 (*dd*, *J* = 9.0, 4.4, H_b–C(10)), and 3.64 (COOMe), as well as the ^{13}C signals at δ(C) 101.7 (C(1)), 155.6 (C(3)), 108.3 (C(4)), 75.6 (C(6)), 132.0 (C(7)), 146.4 (C(8)), 63.9 (C(10)), 169.6 (C(11)), and 51.2 (C(12)) were attributed to the iridoid skeleton of 6α-hydroxygenipin. The positions of attachment of the β-glucopyranosyl unit and the caffeoyl group were determined, respectively, by the following HMBC experiments: H–C(6′)/C(1″) and H–C(1′)/C(1) (*Fig. 2*). From the above data, the structure of **2** was elucidated as 6′-*O*-[(*E*)-caffeoyl]deacetylasperuloside acid methyl ester[1]).

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[1]) For systematic names of **1**–**3**, see *Exper. Part.*

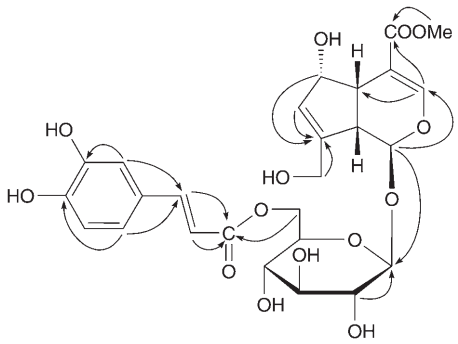

Fig. 2. *Selected HMBC* (H → C) *correlations of* **2**

Table 2. *^{1}H- and ^{13}C-NMR Data of* **2** *and* **3** *at 500 and 125 MHz, Respectively, in CD_3OD.* Chemical shifts δ in ppm, J in Hz.

	2		**3**	
	δ(H)	δ(C)	δ(H)	δ(C)
H–C(1)	5.00 (*d*, *J* = 8.9)	101.7 (*d*)	5.11 (*d*, *J* = 7.6)	97.0 (*d*)
H–C(3)	7.55 (*s*)	155.6 (*d*)	7.14 (br. *s*)	153.9 (*d*)
C(4)	–	108.3 (*s*)	–	112.4 (*s*)
H–C(5)	2.95–2.96 (*m*)	42.6 (*d*)	3.04 (*d*, *J* = 8.4)	31.6 (*d*)
H–C(6)	4.70 (*d*, *J* = 15.6)	75.6 (*d*)	1.83–1.84 (*m*)	41.0 (*d*)
H–C(7)	5.95 (*s*)	132.0 (*d*)	4.27–4.30 (*m*)	73.9 (*d*)
C(8)	–	146.4 (*s*)	–	152.2 (*s*)
H–C(9)	2.56 (*dd*, *J* = 8.1, 8.1)	46.6 (*d*)	2.83–2.84 (*m*)	44.9 (*d*)
CH_2(10)	4.99 (*dd*, *J* = 9.0, 4.4), 4.77 (*dd*, *J* = 9.0, 4.4)	63.9 (*t*)	5.15 (br. *d*, *J* = 7.7)	112.7 (*t*)
C(11)	–	169.6 (*s*)	–	169.5 (*s*)
Me(12)	3.64 (*s*)	51.2 (*q*)		
H–C(1′)	4.64 (*d*, *J* = 7.8)	101.0 (*d*)	4.57 (*d*, *J* = 7.8)	101.1 (*d*)
H–C(2′)	3.14–3.18 (*m*)	75.2 (*d*)	3.14–3.18 (*m*)	74.9 (*d*)
H–C(3′)	3.14–3.18 (*m*)	78.7 (*d*)	3.31–3.35 (*m*)	78.5 (*d*)
H–C(4′)	3.14–3.18 (*m*)	71.7 (*d*)	3.25–3.28 (*m*)	71.5 (*d*)
H–C(5′)	3.30–3.31 (*m*)	78.1 (*d*)	3.46–3.49 (*m*)	75.9 (*d*)
CH_2(6′)	3.77 (*dd*, *J* = 12.3, 1.9), 3.56 (*dd*, *J* = 12.3, 5.1)	63.2 (*t*)	4.41 (*dd*, *J* = 12.3, 1.9), 4.38 (*dd*, *J* = 12.3, 5.1)	64.4 (*t*)
C(1″)	–	169.1 (*s*)	–	167.6 (*s*)
H–C(2″)	6.21 (*d*, *J* = 15.8)	115.1 (*d*)	6.37 (*d*, *J* = 15.8)	115.5 (*d*)
H–C(3″)	7.49 (*d*, *J* = 15.8)	147.6 (*d*)	7.53 (*d*, *J* = 15.8)	146.2 (*d*)
C(4″)	–	127.9 (*s*)	–	125.3 (*d*)
H–C(5″)	6.96 (*d*, *J* = 1.3)	115.5 (*d*)	6.81 (br. *d*)	107.0 (*d*)
C(6″)	–	147.0 (*s*)	–	149.7 (*s*)
C(7″)	–	149.9 (*s*)	–	140.8 (*s*)
H–C(8″)	6.70 (*d*, *J* = 8.2)	116.8 (*d*)	–	149.7 (*d*)
H–C(9″)	6.87 (*dd*, *J* = 8.2, 1.3)	123.3 (*d*)	6.81 (br. *d*)	107.0 (*d*)
*Me*O–C(6″)			3.77 (*s*)	56.6 (*q*)
*Me*O–C(8″)			3.77 (*s*)	56.6 (*q*)

Compound **3**, a pale yellow powder, has a molecular formula of $C_{27}H_{32}O_{14}$ based on its positive-ion HR-ESI-MS (*m/z* 603.16856 ($C_{27}H_{32}NaO_{14}^{+}$; calc. 603.16843). The IR spectrum revealed the absorption bands of OH (3438 cm^{-1}) and C=O (1635 cm^{-1}) groups. The ^{1}H- and ^{13}C-NMR, HMQC, and HMBC spectra showed that **3** consisted of a gardoside moiety esterified to a sinapoyl group. The ^{1}H- and ^{13}C-NMR data of **3** (*Table 2*) showed signals of a sinapoyl group (δ(H) 6.37 (*d*, *J* = 15.8, 1 H), 7.53 (*d*, *J* = 15.8, 1 H), 3.77 (*s*, 2 MeO), 6.81 (*s*, 2 H); δ(C) 167.6, 115.5, 146.2, 125.3, 107.0, 149.7, 140.8, 56.6). The signals at δ(H) 5.11 (*d*, *J* = 7.6, H–C(1)), 7.14 (br. *s*, H–C(3)), 4.27–4.30 (*m*, H–C(7)), and 5.15 (br. *d*, *J* = 7.7, CH_2(10)); as well as the ^{13}C signals at δ(C) 97.0 (C(1)), 153.9 (C(3)), 112.4 (C(4)), 73.9 (C(7)), 152.2 (C(8)), 112.7 (C(10)), and 169.5 (C(11)) were attributed to the iridoid skeleton. The anomeric signal at δ(H) 4.57 (*d*, *J* = 7.8, 1 H) and the signals in the region δ(H) 3.16–3.66, together with the relevant ^{13}C-NMR resonances, indicated the presence of a β-glucopyranosyl unit. The locations of the sinapoyl group at C(6′) and β-D-glucopyranosyl unit at C(1) were established, respectively, by the following HMBC correlations: H–C(6′)/C(1″), H–C(1′)/C(1) and H–C(1)/C(1′) (*Fig. 3*). From the above spectral data and by referencing to those of a known analogue, 6′-*O*-[(*E*)-coumaroyl]gardoside [19], the structure of **3** was elucidated as 6′-*O*-[(*E*)-sinapoyl]gardoside[1]).

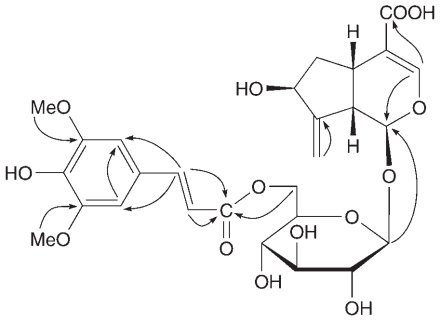

Fig. 3. *Selected HMBC* (H → C) *correlations of* **3**

The configurations of the attached D-glucose moieties of the iriduidal glycosides were tentatively elucidated on the basis of biogenetic consideration (*Figs. 1–3*, and *Tables 1* and *2*).

Experimental Part

General. All chemical solvents used for isolation were of anal. grade. TLC: silica gel *60 PF254* (*Merck*), detected by UV and 10% H_2SO_4/EtOH spraying reagent, followed by heating at 105° for 1–2 min. Column chromatography (CC): Silica gel *H* (200–300 mesh, *Qingdao Ocean Chemical Co., Ltd.*, Qingdao, China), *MCI* gel (*Mitsubishi Chemical Corporation*, Tokyo, Japan), and *Sephadex LH-20* (*Amersham Biosciences*, *GE Health Care*, Sweden) HPLC: *Agilent 1100* system equipped with an *Agilent DAD* spectrophotometer and an auto-sampler; columns were *RP-18* (*Alltima*, *C-18*, 5 μm, 10 × 250 mm) for semi-prep. separations; *Agilent zorbax* (*C-18*, 5 μm, 4.6 × 250 mm) for anal. separation. Optical rotations: *Perkin-Elmer 341* polarimeter in MeOH at 22°. UV Spectra: in MeOH on a *Shimadzu UV-240* spectrophotometer. IR Spectra: *Nicolet FT-IR 380* spectrometer. NMR Spectra: at 500 MHz for ^{1}H and at 125 MHz for ^{13}C on a *Bruker AV-500* spectrometer, using either CD_3OD (for **2** and **3**) or (D_5)pyridine

(for **1**); chemical shifts δ in ppm and coupling constants J in Hz; the ^{1}H,^{1}H-COSY, HSQC, and HMBC spectra were obtained using the standard pulse sequences (XWIN-NMR 3.0). ESI-MS and HR-ESI-MS: *LCQ Deca XP^{plus}* (*Thermo Finnigan*) and *Finigan MAT 95* spectrometers, resp.

Plant Material. The fruits of *Gardenia jasminoides* ELLIS were collected from Jiangxi Province, P. R. China, in October 2005 by *Xiao-Lan Chou*, Professor of Jiangxi College of Traditional Chinese Medicine, and identified by *Cui-Sheng Fan*, Professor of the same college, and kindly provided for this project. A voucher specimen (GJ051006) had been deposited with Shanghai R&D Centre for Standardization of Chinese Medicines, Shanghai, P. R. China.

Extraction and Isolation. The air-dried and powdered fruits of *Gardenia jasminoides* (20 kg) were extracted with 80% EtOH (2×100 l) at 90° under reflux for 2.0 h each. Then, EtOH was removed by evaporation under reduced pressure. The resulting residue (3.05 kg) was suspended in H_2O (6 l), and then partitioned successively with petroleum ether (1×3.6 l, 2×2.4 l), AcOEt (1×3.6 l, 2×2.4 l), and BuOH (1×3.6 l, 2×2.4 l). The BuOH fraction (812 g) was chromatographed over silica gel (15.2×100 cm) with gradient mixtures of $CHCl_3$/MeOH (from 10:1 to 1:1) to yield four major *Fractions* (*Fr. 1–4*). *Fr. 1* was chromatographed on a silica-gel column ($CHCl_3$/MeOH, 20:1) to afford compound **5** (102.5 mg). *Fr. 2* was first separated by *MCI* gel eluted with MeOH/H_2O 0:1 to 1:0 to yield five fractions, *Fr. 2a–2e*. *Fr. 2b* was submitted to repeated CC (silica gel; $CHCl_3$/MeOH 15:1, and *Sephadex LH-20*; MeOH), followed by semi-prep. HPLC (MeOH/H_2O 15:85, 2.0 ml/min) to yield compounds **4** (27 mg; t_R 40.2 min), **6** (18 mg, t_R 17.6 min), and **7** (12 mg, t_R 28.5 min). *Fr. 2c* gave rise to compounds **1** (15 mg), **2** (30 mg), **3** (8 mg), **8** (25 mg), **9** (12 mg), and **10** (35 mg).

4″-O-*[(*E*)*-p-*Coumaroyl]gentiobiosylgenipin* (= *Methyl (1*S*,4a*S*,7a*S*)-1,4a,5,7a-Tetrahydro-7-(hydroxymethyl)-1-[(6-*O*-{4-*O*-[(2*E*)-3-(4-hydroxyphenyl)prop-2-enoyl]-β-*D*-glucopyranosyl}-β-*D*-glucopyranosyl)oxy]cyclopenta[*c*]pyran-4-carboxylate*; **1**). Pale yellow powder. $[\alpha]_D^{22} = -7.08$ ($c = 0.25$, MeOH). UV (MeOH): 232 (4.24), 311 (4.02). IR (KBr): 3411, 2923, 1697, 1631, 1604, 1514, 1439, 1375, 1282, 1163, 1075, 896, 833, 768, 532. ^{1}H- and ^{13}C-NMR: see *Table 1*. HR-ESI-MS (pos.): 719.21683 ($[M + Na]^+$; calc. 719.21577).

6′-O-*[(*E*)-Caffeoyl]deacetylasperuloside Acid Methyl Ester* (= *Methyl (1*S*,4a*S*,5*S*,7a*S*)-1-({6-*O*-[(2*E*)-3-(3,4-Dihydroxyphenyl)prop-2-enoyl]-β-*D*-glucopyranosyl}oxy)-1,4a,5,7a-tetrahydro-5-hydroxy-7-(hydroxymethyl)cyclopenta[*c*]pyran-4-carboxylate*; **2**). Pale yellow powder. $[\alpha]_D^{22} = -7.36$ ($c = 0.25$, MeOH). UV (MeOH): 234 (4.26), 324 (4.46). IR (KBr): 3426, 2924, 1693, 1632, 1522, 1441, 1384, 1279, 1162, 1077, 896, 787, 555. ^{1}H- and ^{13}C-NMR: see *Table 2*. HR-ESI-MS (pos.): 589.15350 ($[M + Na]^+$; calc. 589.15278).

6′-O-[(*E*)*-Sinapoyl]gardoside* (= *(1*S*,4a*S*,6*S*,7a*S*)-1,4a,5,6,7,7a-Hexahydro-6-hydroxy-1-({6-*O*-[(2*E*)-3-(4-hydroxy-3,5-dimethoxyphenyl)prop-2-enoyl]-β-*D*-glucopyranosyl}oxy)-7-methylidenecyclopenta[*c*]pyran-4-carboxylic Acid*; **3**). Pale yellow powder. $[\alpha]_D^{22} = -5.76$ ($c = 0.25$, MeOH). UV (MeOH): 234 (4.14), 326 (4.64). IR (KBr): 3438, 2923, 1635, 1558, 1516, 1456, 1404, 1258, 1157, 577. ^{1}H- and ^{13}C-NMR: see *Table 2*. HR-ESI-MS (pos.): 603.16856 ($[M + Na]^+$; calc. 603.16843).

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