Phenyl and Phenylethyl Glycosides from *Picrorhiza scrophulariiflora*

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Three new phenyl glycosides, scrophenoside A (**1**), B (**2**), and C (**3**), and two new phenylethyl glycosides, scroside D (**4**) and scroside E (**5**), were isolated from the stem of *Picrorhiza scrophulariiflora* PENNELL (Scrophularlaceae), besides five known compounds. On the basis of spectroscopic evidence, the structures of the new compounds were elucidated as 4-acetyl-2-methoxyphenyl 6-*O*-[4-(*β*-D-glucopyranosyloxy)vanilloyl]-*β*-D-glucopyranoside (**1**), 4-acetylphenyl 6-*O*-[(*E*)-*p*-coumaroyl]-*β*-D-glucopyranoside (**2**), 4-[(1*R*)- and (1*S*)-1-hydroxyethyl]-2-methoxyphenyl *β*-D-glucopyranoside (**3a** and **3b**, resp.), 2-(3,4-dihydroxyphenyl)ethyl *O*-*β*-D-glucopyranosyl-(1→3)-4-*O*-[(*E*)-feruloyl]-*β*-D-glucopyranoside (**4**), and 2-(3,4-dihydroxyphenyl)ethyl *O*-*β*-D-glucopyranosyl-(1→3)-6-*O*-[(*E*)-feruloyl]-*β*-D-glucopyranoside (**5**).

Introduction. – *Picrorhiza scrophulariiflora* PENNELL and *Picrorhiza kurrooa* ROYLE *ex* BENTH (Scrophularlaceae) are extensively used in traditional medicine of China, Nepal, and India for the treatment of various immune-system-related diseases. For instance, both plants are used in asthma, jaundice, and arthritis [1]. Previous phytochemical investigation of this plant revealed the presence of iridoid glycosides, cucurbitacins, cucurbitacin glycosides, and phenyl glycosides [2–5]. In this paper, we describe the isolation and identification of three new phenyl glycosides and two new phenylethyl glycosides as well as of five known compounds, androsin (**6**) [4][6], hemiphroside A (**7**) [7], coniferin (**8**) [8], 6-*O*-cinnamoyl-D-glucopyranose (**9**) [9], and 6-*O*-(*p*-coumaroyl)-D-glucopyranose (**10**) [10], which were isolated from the EtOH extract of the stems of *Picrorhiza scrophulariiflora*.

Results and Discussion. – Scrophenoside A (**1**) was obtained as a white amorphous powder. Its molecular formula was determined as $C_{29}H_{36}O_{16}$ by HR-FAB-MS ($[M-H]^-$ at *m/z* 639.1926, calc. 639.1925). The IR absorption indicated the presence of a carbonyl group, an ester group (1704, 1678 cm^{-1}), and an aromatic ring (1593, 1512, 1465, 1418 cm^{-1}). The structure of **1** (*Fig. 1*) was established by ^{1}H- and ^{13}C-NMR data, DEPT, HSQC, HMBC, and tandem MS experiments as 4-acetyl-2-methoxyphenyl 6-*O*-[4-(*β*-D-glucopyranosyloxy)vanilloyl]-*β*-D-glucopyranoside[1]).

The ^{1}H-NMR spectrum of **1** showed the presence of two 1,2,4-trisubstituted benzene rings, which was confirmed by two *ABX* systems at *δ* 7.14–7.52 for six aromatic protons (*δ* 7.44 (*d*, *J* = 1.6 Hz), 7.30 (*dd*, *J* = 1.6, 8.5 Hz), 7.14 (*d*, *J* = 8.5 Hz); *δ* 7.45 (*d*, *J* = 1.7 Hz), 7.52 (*dd*, *J* = 1.7, 8.5 Hz), 7.18 (*d*, *J* = 8.5 Hz)). A comparison of the ^{1}H- and ^{13}C-NMR data with those of **6** and vanillic acid (= 4-hydroxy-3-methoxybenzoic acid) suggested that the two 1,2,4-trisubstituted benzene rings were part of an androsin and a vanilloyl moiety. In addition, two

[1]) Arbitrary numbering; for systematic names, see *Exper. Part*

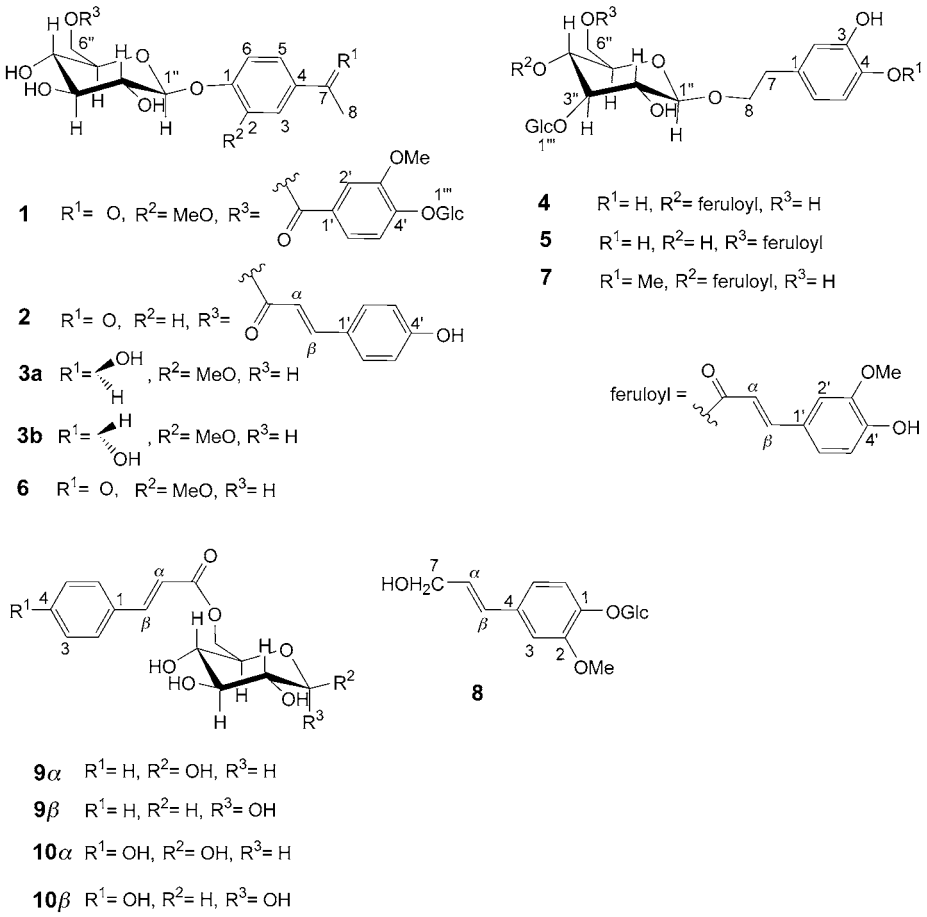

Fig. 1. *Structure of compounds* **1**–**10**[1])

anomeric protons were observed at δ 5.13 ($d, J = 7.2$ Hz) and 5.04 ($d, J = 7.2$ Hz) indicating the diglycosidic structure of **1**, which was also confirmed by the ^{13}C-NMR spectrum of **1** (δ 100.16 and 99.7; *Table*). To determine their connectivities, HMBC and tandem ESI-MS experiments were employed. As shown in *Fig. 2*, the long-range correlations of the two anomeric protons (δ 5.13 and 5.04) with C(1) (δ 150.93) and C(4′) (δ 151.42), respectively, indicated that two glucose units were connected with C(1) and C(4′)[1]). Likewise, the correlations of CH_2(6″) with C=O (δ 165.76) enabled us to assign the position of the vanilloyl group to C(6″) of glucose. The structure of **1** was further confirmed by an ESI-MS^n experiment. MS^1 gave the pseudomolecular ion at *m/z* 675 ($[M + Cl]^-$), MS^2 the fragment ion at *m/z* 477 ($[M - H - 162]^-$), and MS^3 the fragment ions at *m/z* 311 ($[M - H - 162 - 166]^-$) and 165 ($[M - H - 162 - 166 - 146]^-$), corresponding to the sequential loss of a glucose unit, and the vanillic acid and glucose moieties.

Scrophenoside B (**2**) was isolated as a white amorphous powder. Its molecular formula was determined as $C_{23}H_{24}O_9$ by HR-FAB-MS ($[M - H]^-$ at *m/z* 443.1355, calc. 443.1342). The IR absorption indicated the presence of a carbonyl and an ester group (1693, 1659 cm^{-1}), a C=C bond (1610 cm^{-1}), and an aromatic ring (1582, 1516, 1449 cm^{-1}). Further investigation of 1D- and 2D-NMR data resulted in the

Table 1. *^{13}C-NMR Data* ((D$_6$)DMSO) *for* **1**–**6** *and* **7**. δ in ppm[1]).

	1	**2**	**3a**	**3b**	**4**	**5**	**6**	**7**
C(1)	150.93	161.43	145.76	145.76	129.11	129.87	151.02	130.94
C(2)	149.28[a])	116.49[a])	149.35	149.35	116.28	116.96	149.49	116.19
C(3)	111.66	130.86	110.47	110.52	144.96	145.62	111.90	145.98
C(4)	131.51	131.49	141.98	141.98	143.51	144.17	131.74	144.72
C(5)	122.87	130.86	117.88	117.88	115.40	116.08	123.11	112.17
C(6)	114.75	116.49[a])	115.76	115.76	119.54	120.15	114.82	119.30
C(7)	197.13	197.00	68.47	68.51	34.98	35.80	197.36	34.86
C(8)	27.08	26.89	26.69	26.69	70.12	70.80	27.19	69.90
MeO	56.25[b])	–	56.25	56.25	–	–	56.26	55.50
C(1′)	123.62	125.69	100.85	100.91	125.78	126.21	–	125.71
C(2′)	113.43	131.00	73.89	73.89	110.98	111.70	–	110.84
C(3′)	149.25[a])	116.50[a])	77.64	77.64	147.84	148.62	–	147.80
C(4′)	151.42	160.57	70.34	70.34	149.35	150.04	–	149.08
C(5′)	114.97	131.00	77.53	77.53	115.42	116.13	–	115.36
C(6′)	123.58	116.50[a])	61.34	61.34	123.02	124.10	–	122.98
C=O	165.76	167.00	–	–	165.84	167.28	–	165.78
C(α)	–	114.69	–	–	114.84	114.88	–	114.63
C(β)	–	145.51	–	–	144.76	145.99	–	144.72
MeO	56.41[b])	–	–	–	55.59	56.40	–	55.59
C(1″)	100.16	100.12	–	–	102.11	102.86	100.16	102.03
C(2″)	73.64	73.72	–	–	74.57[a])	72.77	74.04	74.51
C(3″)	77.30	77.00	–	–	82.91	88.31	77.31	82.85
C(4″)	70.70	70.67	–	–	69.30	69.15	70.71	69.27
C(5″)	74.58	74.53	–	–	74.36[a])	73.82	77.83	74.26
C(6″)	64.62	63.94	–	–	60.94	63.87	61.65	60.86
C(1‴)	99.70	–	–	–	104.48	104.74	–	104.44
C(2‴)	73.74	–	–	–	73.26	74.50	–	73.19
C(3‴)	77.73	–	–	–	76.28	76.71	–	76.22
C(4‴)	70.14	–	–	–	69.88	70.82	–	69.79
C(5‴)	77.51	–	–	–	76.88	77.59	–	76.84
C(6‴)	61.19	–	–	–	60.75	61.74	–	60.68

[a]) [b]) Signals in each vertical column are interchangeable.

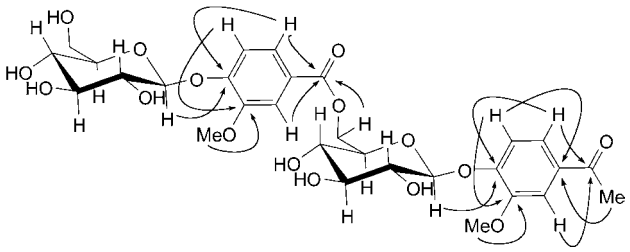

Fig. 2. *Key HMBC correlations of* **1**

determination of the structure of **2** as 4-acetylphenyl 6-*O*-[(*E*)-*p*-coumaroyl]-β-D-glucopyranoside[1]) (*p*-coumaric acid = (2*E*)-3-(4-hydroxyphenyl)-prop-2-enoic acid).

The ^{1}H-NMR spectrum of **2** exhibited two *AA′BB′* systems (δ 7.84 (*d*, *J* = 8.4 Hz, 2 H), 7.09 (*d*, *J* = 8.4 Hz, 2 H); δ 7.54 (*d*, *J* = 8.4 Hz, 2 H), 6.79 (*d*, *J* = 8.4 Hz, 2 H), a Me group (δ 2.37 (*s*)), an (*E*)-double bond (δ 7.53

(d, J = 15.9 Hz, 1 H), 6.38 (d, J = 15.9 Hz, 1 H), and an anomeric proton (δ 5.06 d, J = 7.2 Hz, 1 H). Combined with the ^{13}C-NMR data (*Table*), these data suggested that **2** was a phenyl glycoside containing two 1,4-disubstitued benzene rings. In the HMBC spectrum, the anomeric proton H–C(1″) showed correlation with C(1), and the correlation of CH_2(6″) with C=O (δ 167.00) was also observed[1]). Thus we concluded that an ester group was connected with C(6″) of the glucose unit. The structure of **2** was further supported by the ESI-MS^n analysis. MS^1 gave the quasimolecular ion at m/z 443 ($[M-H]^-$, MS^2 the fragment ion at m/z 307 ($[M-H-136]^-$), and MS^3 the fragment ions at m/z 163 and 145.

Scrophenoside C (**3**), an amorphous powder, was isolated as a diastereoisomer mixture **3a**/**3b**. Its molecular formula was determined as $C_{15}H_{22}O_8$ by HR-FAB-MS ($[M-H]^-$ at m/z 329.1265, calc. 329.1236). On the basis of spectral evidence and chemical transformation, compound **3** was identified as 4-[(1*R*)- and (1*S*)-1-hydroxyethyl]-2-methoxyphenyl β-D-glucopyranoside.

The ^{1}H- and ^{13}C-NMR data of **3** showed the presence of a glucose, and a 1,2,4-trisubstitued benzene ring. In the ^{1}H-NMR spectrum, a Me signal was present at δ 1.29 (d, J = 6.3 Hz), a CH resonance at δ 4.63 (q, J = 6.3 Hz), a MeO signal at δ 3.72 (s), and an anomeric proton at δ 4.82 (d, J = 7.2 Hz, 1 H). In the HMBC spectrum (*Fig. 3*), the correlations further confirmed the structure of **3**. Furthermore, in the ^{13}C-NMR spectra (*Table*), C(7), C(3), and C(1) appeared as split signals, so we concluded that **3** might be a mixture of (7*R*) and (7*S*)-diastereoisomers[1]). To confirm this deduction, we reduced androsin (**6**) with $NaBH_4$ to a diastereoisomer mixture which was identical to scrophenoside C (**3**) (by ^{13}C-NMR and TLC).

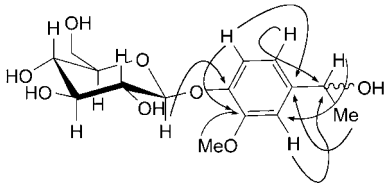

Fig. 3. *Key HMBC correlations for* **3**

Scroside D (**4**), a yellow amorphous powder, was determined as $C_{30}H_{38}O_{16}$ by HR-FAB-MS ($[M-H]^-$ at m/z 653.2099, calc. 653.2082). The ^{1}H- and ^{13}C-NMR spectra of **4** (see *Exper. Part* and *Table*) were similar to those of the known compound **7** [7], except for the absence of 1 MeO group at C(4), indicating that **4** might be 2-(3,4-dihydroxyphenyl)ethyl *O*-β-D-glucopyranosyl-(1 → 3)-4-*O*-[(*E*)-feruloyl]-β-D-glucopyranoside[1]) (ferulic acid = (2*E*)-3-(4-hydroxy-3-methoxyphenyl)prop-2-enoic acid). The DEPT, HSQC, HMBC, and ESI-MS-MS data confirmed the structure of **4**.

The long-range correlation of C(3′) (δ 147.84) with MeO (δ 3.80) (*Fig. 4*) and the fragment ion at m/z 477 ($[M-177]^-$, in the ESI-MS-MS (MS^2) of **4** indicated the presence of a feruloyl group. Also the correlations of the ester C=O with H–C(4″), of C(3″) (δ 82.91) with H–C(1‴) (δ 4.37), and of C(8) (δ 70.12) with H–C(1″) (δ 4.39) were also observed.

Scroside E (**5**) was isolated as a yellow amorphous powder. Its HR-FAB-MS spectrum ($[M-H]^-$ at m/z 653.2080, calc. 653.2082) indicated that it had the same molecular formula as **4** ($C_{30}H_{38}O_{16}$). The ^{1}H- and ^{13}C-NMR spectra of **5** were similar to those of **4**, and detailed analysis of the HSQC, HMBC, and tandem ESI-MS data as well as the hydrolysis results suggested that **5** was an isomer of **4**; *i.e.*, 2-(3,4-dihydroxyphenyl)ethyl *O*-β-D-glucopyranosyl-(1 → 3)-6-*O*-[(*E*)-feruloyl]-β-D-glucopyranoside[1]).

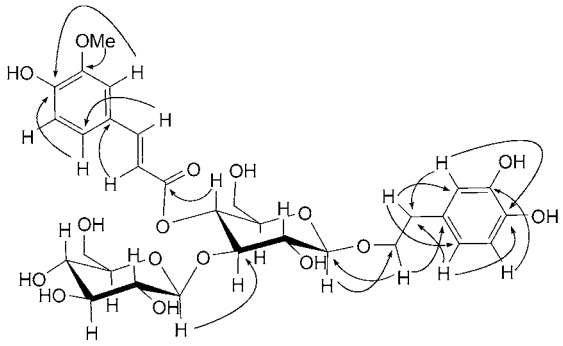

Fig. 4. *Key HMBC correlations for* **4**

The ^{1}H-NMR spectrum of **5** showed a marked upfield shift (δ 3.34) of H–C(4″) and significant downfield shifts (δ 4.21 and 4.39) of CH_2(6″) for glucose, compared with the corresponding signals of **4** suggesting that the feruloyl moiety should be connected to C(6″). Moreover, the long-range correlations of the ester C=O with CH_2(6″) in the HMBC spectrum of **5** further confirmed the position of the feruloyl at C(6″) of the glucose unit. On hydrolysis of **5**, only β-D-glucose was obtained (by TLC).

All known compounds were identified by comparing their physical and spectral data with literature values. The main constituent of *P. scrophulariiflora*, androsin (**6**), which was also isolated from *P. kurrooa*, was shown to possess anti-asthma activities [11]. The structure of the new compounds scrophenoside A (**1**), B (**2**), and C(**3**) are similar to androsin; thus they may be the bioactive anti-asthma components in *P. scrophulariiflora*. In addition, phenylethyl glycosides, which were abundant in this plant but had not been found in *P. kurrooa*, seem to be the characteristic constituents in the genus of *P. scrophulariiflora*.

Experimental Part

General. Column chromatography (CC): *Sephadex LH-20* (*Pharmacia*), silica gel (200–300 mesh; *Qingdao Marine Chemical Group Co.*), *Lobar LiChroprep RP-18* (40–63 μm, *Merck*), *Lobar LiChroprep Si-60* (40–63 μm, *Merck*), and *MCI*-gel *CHP-20P* (75–150 μm, *Mitsubishi Chemical Co.*). Optical rotations: *Perkin-Elmer 341* polarimeter. IR Spectra: *Perkin-Elmer Spectrum-One* FT-IR spectrometer; $\tilde{\nu}$ in cm^{-1}. NMR Spectra: *Bruker AV-600* spectrometer; δ in ppm rel. to $SiMe_4$ as internal standard, *J* in Hz. MS: *VGAutoSpec 3000* spectrometer for HR-FAB and *Finnigan LCQ-Deca* for ESI-MS and tandem spectra.

Plant Material. The dried stems of *Picrorhiza scrophulariiflora* were collected from Tibet and identified by Prof. *Zhao Zuo-Cheng*. A voucher specimen was deposited in the Herbarium of Chengdu Institute of Biology, Chinese Academy of Sciences.

Extraction and Isolation. The dried stems of *Picrorhiza scrophulariiflora* (6 kg) were powdered and extracted with EtOH at 60° (3 × 8 h). After filtration, the solvent was evaporated to give 2 kg of extract. The extract was suspended in H_2O and extracted with $CHCl_3$ and AcOEt/MeOH 10:1. The latter extract (50 g) was submitted to CC (silica gel, $CHCl_3$/MeOH of increasing polarity): *Fractions 1–4*. *Fr. 1* (5 g) was subjected to CC (ODS gel, MeOH/H_2O 5:1, 3:1, and 1:1): *Fr. 1.1–1.3*. Every fraction was submitted to CC (*RP-18*): **6** (500 mg), **9** (= **9α**/**9β**) (14 mg), and **2** (15 mg), after purification by CC (*Sephadex LH-20* MeOH). *Fr. 2* (25 g) was separated by CC (*MCI*-gel MeOH/H_2O gradient 1:5 → 8:1): *Fr. 2.1–2.7*. *Fr. 2.2* afforded **3** (10 mg) and **8** (60 mg) after CC (silica gel (*Si-60*), AcOEt/MeOH 15:1). *Fr. 2.4* was submitted CC (*RP-18*): **10** (= **10α**/**10β**) (12 mg). *Fr. 2.6* was submitted to CC (silica gel $CHCl_3$/MeOH 8:1): **7** (35 mg). *Fr. 3* (10 g) was separated by CC (silica gel, AcOEt/MeOH 20:1 → 5:1): *Fr. 3.1–3.15*. *Fr. 3.3* yielded **1** (11 mg), and *Fr. 3.5* was submitted to CC (*RP-18*, MeOH/H_2O 1:3): **4** (9 mg) and **5** (8 mg), after further purification by CC (*Sephadex LH-20*, MeOH).

Scrophenoside A (=*1-[4-(β-*D*-Glucopyranosyloxy)-3-methoxyphenyl]ethanone 6-[4-(β-*D*-Glucopyranosyloxy)-3-methoxybenzoate]*; **1**): White amorphous powder (11 mg). $[\alpha]_D^{25} = -65.1$ ($c = 0.40$, MeOH/H_2O 1:1). IR (KBr): 3390, 2921, 1678, 1593, 1512, 1466, 1419, 1277, 1219, 1072, 1028, 763, ^{1}H-NMR ((D$_6$)DMSO, 600 MHz)[1]): 7.44 (*d*, *J* = 1.6, H−C(2)); 7.30 (*dd*, *J* = 1.6, 8.5, H−C(5)); 7.14 (*d*, *J* = 8.5, H−C(6)); 3.80 (*s*, MeO); 2.47 (*s*, Me(8)); 7.45 (*d*, *J* = 1.7, H−C(2′)); 7.18 (*d*, *J* = 8.5, H−C(5′)); 7.52 (*dd*, *J* = 1.7, 8.5, H−C(6′)); 3.77 (*s*, MeO); 5.13 (*d*, *J* = 7.2, H−C(1″)); 4.22 (*dd*, *J* = 7.5, 11.6, 1 H−C(6″)); 4.58 (*d*, *J* = 11.6, 1 H−C(6″)); 5.04 (*d*, *J* = 7.2, H−C(1‴)); 3.64 (*dd*, *J* = 4.5, 12.0, 1 H−C(6‴)); 3.45 (br. *s*, 1 H−C(6‴)). ^{13}C-NMR: *Table.* HR-FAB-MS: 639.1926 ($[M-H]^-$, $C_{29}H_{35}O_{16}^-$; calc. 639.1925).

Scrophenoside B (=*1-[4-(β-*D*-Glucopyranosyloxy)phenyl]ethanone 6-[(2*E*)-3-(4-Hydroxyphenyl)prop-2-enoate]*; **2**): White amorphous powder (15 mg). $[\alpha]_D^{25} = -40.8$ ($c = 0.41$, MeOH). IR (KBr): 3326, 2927, 1693, 1659, 1610, 1582, 1516, 1449, 1282, 1257, 1066, 1045, 974, 831. ^{1}H-NMR ((D$_6$)DMSO, 600 MHz)[1]): 7.09 (*d*, *J* = 8.4, H−C(2), H−C(6)); 7.84 (*d*, *J* = 8.4, H−C(3), H−C(5)); 2.37 (*s*, Me(8)); 7.54 (*d*, *J* = 8.4, H−C(2′), H−C(6′)); 6.79 (*d*, *J* = 8.4, H−C(3′), H−C(5′)); 6.38 (*d*, *J* = 15.9, H−C(α)); 7.53 (*d*, *J* = 15.9, H−C(β)); 5.06 (*d*, *J* = 7.2, H−C(1″)); 4.22 (*dd*, *J* = 7.5, 11.7, 1 H−C(6″)); 4.58 (*d*, *J* = 11.7, 1 H−C(6″)). ^{13}C-NMR: *Table.* HR-FAB-MS: 443.1355 ($[M-H]^-$, $C_{23}H_{23}O_9^-$; calc. 443.1342).

Scrophenoside C (=*4-(1-Hydroxyethyl)-2-methoxyphenyl β-*D*-Glucopyranoside*; **3**): White amorphous powder (10 mg). $[\alpha]_D^{25} = -47.8$ ($c = 0.11$, MeOH). IR (KBr): 3381, 2934, 1597, 1518, 1469, 1420, 1265, 1074, 1019, 808, 712. ^{1}H-NMR ((D$_6$)DMSO, 600 MHz)[1]): 6.95 (*s*, H−C(2)); 6.80 (*d*, *J* = 8.4, H−C(5)); 6.99 (*d*, *J* = 8.4, H−C(6)); 4.63 (*q*, *J* = 6.3, H−C(7)); 1.29 (*d*, *J* = 6.3, Me(8)); 3.72 (*s*, MeO); 4.82 (*d*, *J* = 7.2, H−C(1″)); 3.44 (*dd*, *J* = 6.0, 11.7, H−C(6″)); 3.64 (*d*, *J* = 11.7, H−C(6″)). ^{13}C-NMR: *Table.* HR-FAB-MS: 329.1265 ($[M-H]^-$, $C_{15}H_{21}O_8^-$; calc. 329.1236).

Scroside D (=*2-(3-Hydroxy-4-methoxyphenyl)ethyl 3-*O*-β-*D*-Glucopyranosyl-β-*D*-glucopyranoside 4-[(2*E*)-3-(4-Hydroxy-3-methoxyphenyl)prop-2-enoate]*; **4**): Yellow amorphous powder (9 mg). $[\alpha]_D^{25} = -44.5$ ($c = 0.4$, MeOH). IR (KBr): 3417, 2932, 1704, 1633, 1592, 1515, 1431, 1273, 1159, 1130, 1071, 1029, 811, 762. ^{1}H-NMR ((D$_6$)DMSO, 600 MHz)[1]): 6.62 (*s*, H−C(2)); 6.62 (*d*, *J* = 8.4, H−C(5)); 6.49 (*d*, *J* = 8.4, H−C(6)); 2.68 (*t*, *J* = 7.4, 2 H−C(7)); 3.88 (*m*, 1 H−C(8)); 3.60 (*m*, 1 H−C(8)); 7.30 (*s*, H−C(2′)); 6.79 (*d*, *J* = 7.7, H−C(5′)); 7.09 (*d*, *J* = 7.7, H−C(6′)); 6.47 (*d*, *J* = 15.6, H−C(α)); 7.51 (*d*, *J* = 15.6, H−C(β)); 3.80 (*s*, MeO); 4.39 (*d*, *J* = 7.8, H−C(1″)); 3.77 (*m*, H−C(3″)); 4.69 (*t*, *J* = 9.6, H−C(4″)); 3.25 (*dd*, *J* = 5.4, 11.5, 1 H−C(6″)); 3.52 (*d*, *J* = 11.5, 1 H−C(6″)); 4.37 (*d*, *J* = 7.8, H−C(1‴)). ^{13}C-NMR: *Table.* HR-FAB-MS: 653.2099 ($[M-H]^-$, $C_{30}H_{37}O_{16}^-$; calc. 653.2082).

Scroside E (=*2-(3-Hydroxy-4-methoxyphenyl)ethyl 3-*O*-β-*D*-Glucopyranosyl-β-*D*-glucopyranoside 6-[(2*E*)-3-(4-Hydroxy-3-methoxyphenyl)prop-2-enoate]*; **5**): Yellow amorphous powder (8 mg). $[\alpha]_D^{25} = -42.5$ ($c = 0.40$, MeOH). IR (KBr): 3407, 2926, 1704, 1634, 1593, 1515, 1431, 1273, 1159, 1071, 1029, 810, 762. ^{1}H-NMR ((D$_6$)DMSO, 600 MHz)[1]): 6.60 (*s*, H−C(2)); 6.80 (*d*, *J* = 8.4, H−C(5)); 6.43 (*d*, *J* = 8.4, H−C(6)); 2.66 (*t*, *J* = 7.4, 2 H−C(7)); 3.77 (*m*, 1 H−C(8)); 3.54 (*m*, 1 H−C(8)); 7.32 (*s*, H−C(2′)); 6.77 (*d*, *J* = 7.8, H−C(5′)); 7.06 (*d*, *J* = 7.8, H−C(6′)); 6.50 (*d*, *J* = 15.9, H−C(α)); 7.53 (*d*, *J* = 15.9, H−C(β)); 3.80 (*s*, MeO); 4.37 (*d*, *J* = 7.8, H−C(1″)); 3.40 (br. *s*, H−C(3″)); 3.34 (br. *d*, H−C(4″)); 4.21 (*dd*, *J* = 6.0, 12.0, 1 H−C(6″)); 4.39 (*d*, *J* = 12.0, 1 H−C(6″)); 4.32 (*d*, *J* = 7.8, H−C(1‴)). ^{13}C-NMR: *Table.* HR-FAB-MS: 653.2080 ($[M-H]^-$, $C_{30}H_{37}O_{16}^-$; calc. 653.2082).

Androsin (=*1-[4-(β-*D*-Glucopyranosyloxy)-3-methoxyphenyl]ethanone*; **6**) [6]. White amorphous solid (500 mg). ^{1}H-NMR ((D$_6$)DMSO, 600 MHz)[1]): 2.47 (*s*, COMe); 3.83 (*s*, MeO); 5.11 (*d*, *J* = 7.2, H−C(1″)); 7.13 (*d*, *J* = 8.4, H−C(6)); 7.32 (*dd*, *J* = 8.4, 1.6, H−C(5)); 7.45 (*d*, *J* = 1.6, H−C(3)). ^{13}C-NMR ((D$_6$)DMSO, 150 MHz)[1]): 151.89 (C(1)); 150.03 (C(2)); 11.44 (C(3)); 131.74 (C(4)); 123.20 (C(5)); 114.82 (C(6)); 196.36 (C(7)); 26.19 (C(8)). ESI-MS (neg.): 327 ($[M-H]^-$).

Hemiphroside A (=*2-(3-Hydroxy-4-methoxyphenyl)ethyl 3-*O*-β-*D*-Glucopyranosyl-β-*D*-glucopyranoside 4-[(2*E*)-3-(4-Hydroxy-3-methoxyphenyl)prop-2-enoate]* **7**) [7]. Yellow amorphous powder (35 mg). $[\alpha]_D^{25} = -46.8$ ($c = 0.34$, MeOH). ^{1}H-NMR ((D$_6$)DMSO, 600 MHz)[1]): 6.68 (*s*, H−C(2)); 6.81 (*d*, *J* = 8.4, H−C(5)); 6.63 (*d*, *J* = 8.4, H−C(6)); 2.72 (*t*, *J* = 7.4, 2 H−C(7)); 3.90 (*m*, 1 H−C(8)); 3.62 (*m*, 1 H−C(8)); 3.72 (*s*, MeO); 7.31 (*s*, H−C(2′)); 6.78 (*d*, *J* = 7.8, H−C(5′)); 7.10 (*d*, *J* = 7.8, H−C(6′)); 6.48 (*d*, *J* = 15.9, H−C(α)); 7.52 (*d*, *J* = 15.9, H−C(β)); 3.81 (*s*, MeO); 4.40 (*d*, *J* = 7.8, H−C(1″)); 4.70 (*t*, *J* = 9.6, H−C(4″)); 4.37 (*d*, *J* = 7.8, H−C(1‴)). ^{13}C-NMR: *Table.* ESI-MS (neg.): 667 ($[M-H]^-$).

Coniferin (=*4-[(1*E*)-3-Hydroxyprop-1-enyl]-2-methoxyphenyl β-*D*-Glucopyranoside*; **8**) [8]. White amorphous powder (60 mg). $[\alpha]_D^{25} = -68.3$ ($c = 0.1$, H_2O). ^{1}H-NMR ((D$_6$)DMSO, 600 MHz)[1]): 7.05 (*d*, *J* = 1.4, H−C(3)); 7.00 (*d*, *J* = 8.4, H−C(6)); 6.88 (*dd*, *J* = 8.4, 1.4, H−C(5)); 6.46 (*d*, *J* = 15.8, H−C(α)); 6.27 (*dt*, *J* = 15.8, 5.2, H−C(β)); 4.88 (*d*, *J* = 7.2, H−C(1′)); 4.09 (br., 2 H−C(7)). ^{13}C-NMR ((D$_6$)DMSO, 150 MHz)[1]):

149.66 (C(2)); 146.63 (C(1)); 131.62 (C(4)); 129.64 (C(β)); 129.05 (C(α)); 119.66 (C(5)); 115.83 (C(6)); 110.45 (C(3)); 100.6 (C(1′)); 62.26 (C(7)); 56.26 (MeO). ESI-MS (neg.): 341 ([$M-H$]$^-$).

D-*Glucopyranose 6-[(2*E*)-3-Phenylprop-2-enoate]* (**9**) [9]. White amorphous powder (14 mg). ^{1}H-NMR (CD_3OD, 600 MHz): glucose moiety: 5.15 (*d*, *J* = 3.6, H–C(1), α-D); 4.55 (*d*, *J* = 7.8, H–C(1), β-D). ^{13}C-NMR ((D_6)DMSO, 150 MHz)[1]): cinnamoyl moiety: 167.84, 167.78 (C=O); 145.70, 145.67 (C(α)); 134.36 (C(1)); 130.62 (C(4)); 128.97 (C(3)); 128.14 (C(2)); 117.30, 117.26 C(β)); glucose moiety: 96.92 (C(1), β-D); 73.49 (C(2), β-D); 76.59 (C(3), β-D); 70.66 (C(4), β-D); 74.10 C(5), β-D); 63.95 (C(6), β-D); 92.76 (C(1), α-D); 74.91 C(2), α-D); 72.43 (C(3), α-D); 69.56 (C(4), α-D); 70.46 (C(5), α-D); 63.91 (C(6), α-D). ESI-MS (neg.): 309 ([$M-H$]$^-$).

D-*Glucopyranose 6-[(2*E*)-3-(4-Hydroxyphenyl)prop-2-enoate]* (**10**) [10]. White amorphous powder (12 mg). ^{1}H-NMR ((D_6)DMSO, 600 MHz)[1]): glucose moiety: 4.91 (*d*, *J* = 4.1, H–C(1), α-D); 4.31 (*d*, *J* = 7.3, H–C(1), β-D); *p*-coumaroyl moiety: 6.78 (*d*, *J* = 8.6, H–C(2), H–C(6)); 7.54 (*d*, *J* = 8.6, H–C(3), H–C(5)); 6.39 (*d*, *J* = 15.8, H–C(α)); 7.53 (*d*, *J* = 15.8, H–C(β)). ^{13}C-NMR ((D_6)DMSO, 150 MHz)[1]): *p*-coumaroyl moiety: 167.35 (C=O); 145.62, 145.49 (C(α)); 131.05 (C(2)); 125.72 (C(1)); 116.43 (C(3)); 114.73, 114.62 (C(β)); glucose moiety: 97.58 (C(1), β-D); 73.56 (C(2), β-D); 77.09 (C(3), β-D); 70.88 (C(4), β-D); 75.37 (C(5), β-D); 92.97 (C(1), α-D); 74.25 C(2), α-D); 72.85 C(3), α-D); 69.56 (C(4), α-D); 71.31 (C(5), α-D); 64.69, 64.63 (C(6), α-D and β-D). ESI-MS (neg.): 325 ([$M-H$]$^-$).

TLC Analysis of Sugars of **1**–**5**. Compounds **1**–**5** were each applied to a TLC plate and then hydrolyzed under HCl vapor at 60° for 40 min. After the excess HCl was removed, glucose was applied to the same plate, the plate developed ($CHCl_3$/MeOH/H_2O/AcOH 16:9:2:2), sprayed with aniline/phthalic acid, and heated. Glucose gave a purple spot, R_f 0.42.

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