Two New Iridoids from the Stem of *Catalpa ovata*

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Two new iridoids, 6-*O*-[(*E*)-feruloyl]jioglutin D (**1**) and 6-*O*-(4-hydroxybenzoyl)jioglutin D (**2**), and six known compounds, minecoside (**3**), specioside (**4**), picroside II (**5**), picroside III (**6**), 4-hydroxybenzoic acid (**7**), and martynoside (**8**), were isolated from the stem of *Catalpa ovata*. The structures of the new compounds were established on the basis of spectroscopic techniques, including 1D- and 2D-NMR.

Introduction. – *Catalpa ovata* G. DON (Bignoniaceae), a perennial deciduous tree, is widely distributed in Korea, China, and Japan. The fruits of this plant have been used as a diuretic to treat chronic nephritis and edema. The root and stem barks also have been used for the treatment of pyrexia, jaundice, and edema by nephritis [1][2]. The plants of this genus are reported to be rich of iridoids [3–5], naphthoquinones [6–9], and monoterpene glycosides [10]. As part of our ongoing search for chemical constituents of Bignoniaceae family [11], two new iridoids, 6-*O*-[(*E*)-feruloyl]jioglutin D (**1**) and 6-*O*-(4-hydroxybenzoyl)jioglutin D (**2**), and six known compounds, **3**–**8**, were isolated from the stem of *Catalpa ovata* (*Fig. 1*). Here, we describe the isolation and structure elucidation of the new compounds **1** and **2**.

Results and Discussion. – Compound **1** was obtained as white amorphous powder. The HR-ESI-MS of **1** showed a *quasi*-molecular ion ($[M+Na]^+$) peak at *m*/*z* 445.1478 (calc. 445.1475), consistent with a molecular formula $C_{21}H_{26}O_9$. The ^{1}H- and ^{13}C-NMR (*Table*), DEPT, and HMQC spectra of **1** indicated the presence of two acetal groups (δ(H) 5.05 (*d*, *J* = 3.8, H–C(1)[2]) and 4.83 (*dd*, *J* = 6.1, 2.5, H–C(3)); δ(C) 99.2 and 96.3, resp.), two CH–O groups (δ(H) 5.26 (br. *d*, *J* = 8.3, H–C(6)) and 3.65 (br. *s*, H–C(7)); δ(C) 80.7 and 61.4, resp.), one CH_2–O group (δ(H) 3.60 and 4.08 (2*d*, *J* = 12.5, CH_2(10)); δ(C) 61.2), one CH_2 group (δ(H) 1.92–1.93 and 1.97–1.98 (2*m*, CH_2(4)); δ(C) 30.2), two CH groups (δ(H) 2.32–2.34 (*m*, H–C(5)) and 2.84 (*dd*, *J* = 8.2, 3.8, H–C(9); δ(C) 34.0 and 41.2, resp.), two MeO groups (δ(H) 3.51 (*s*, MeO–C(1)) and

[1]) These authors contributed equally to this work.
[2]) Trivial atom numbering. For systematic names, *cf.* the *Exper. Part.*

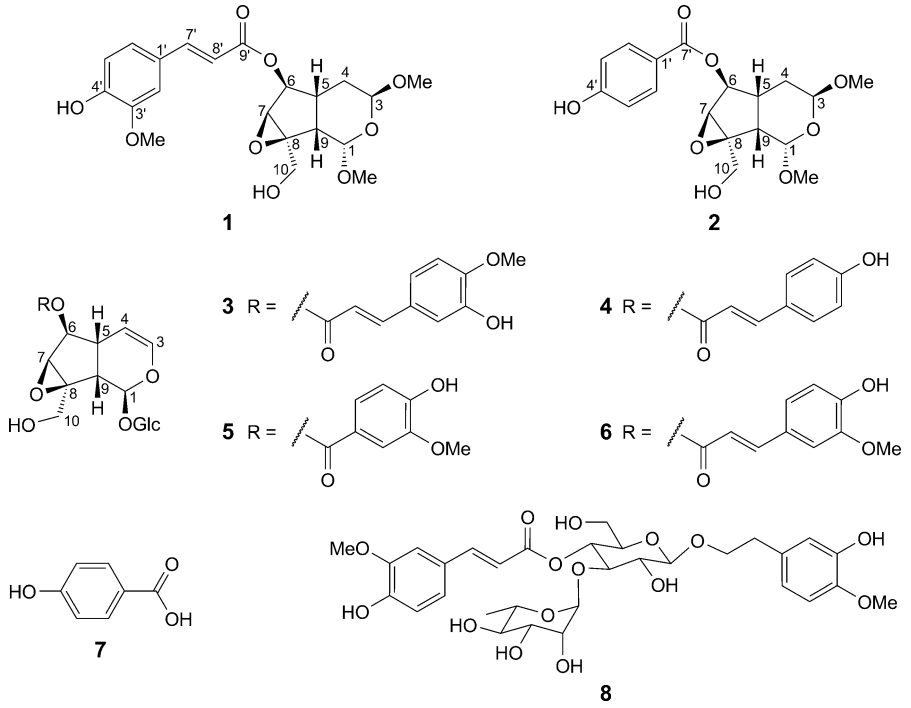

Fig. 1. *Structures of compounds* **1**–**8** *isolated from* C. ovata

3.49 (*s*, MeO–C(3)); δ(C) 55.2 and 55.9, resp.), and one O-bearing quaternary C-atom (δ(C) 67.3), which are characteristic of a C_9-iridoid skeleton containing two acetal groups [12][13]. The remaining data indicated the presence of an (*E*)-feruloyl group (δ(H) 7.28 (*d*, $J = 1.8$, H–C(2′)), 6.88 (*d*, $J = 8.1$, H–C(5′)), 7.16 (*dd*, $J = 8.1$, 1.8, H–C(6′)), 7.72 (*d*, $J = 15.9$, H–C(7′)), 6.46 (*d*, $J = 15.9$, H–C(8′)), and 3.96 (*s*, MeO–C(3′)); δ(C) 127.6, 111.8, 149.5, 151.0, 116.5, 124.3, 147.4, 115.0, 169.3, and 56.5). These data suggested that the structure of **1** was similar to that of jioglutin D [12][13], except for the presence of an (*E*)-feruloyl group. The ^{1}H,^{1}H-COSY spectrum of **1** revealed the partial connectivities of CH(3)–CH_2(4)–CH(5)–CH(6)–CH(7) and CH(5)–CH(9)–CH(1) (*Fig. 2*). The HMBC spectrum of **1** showed the long-range correlations *Me*O–C(1)/C(1), *Me*O–C(3)/C(3), H–C(6)/C(9′), and *Me*O–C(3′)/C(3′), evidencing that the two MeO and an (*E*)-feruloyl group were at C(1), C(3), and C(6), respectively (*Fig. 2*). The NOESY spectrum of **1** showed the significant correlations H–C(1)/H–C(9), H–C(1)/*Me*O–C(3), H–C(5)/H–C(9), H–C(5)/H_b–C(4), H–C(6)/H_a–C(4), and CH_2(10)/*Me*O–C(1). These data indicated that the rings *A* and *B* were *cis*-fused, and H–C(5), H–C(9), *Me*O–C(3), and (*E*)-feruloyl groups were β-oriented, and the *Me*O–C(1) and CH_2(10) groups were in α-orientation (*Fig. 3*). Therefore, the structure of **1** was identified as 6-*O*-[(*E*)-feruloyl]jioglutin D.

Compound **2** was obtained as white amorphous powder. The molecular formula, $C_{18}H_{22}O_8$, was deduced from the HR-ESI-MS data (*m*/*z* 389.1223 ([$M + Na$]$^+$; calc. 389.1212)). The ^{1}H- and ^{13}C-NMR spectra of **2** were quite similar to those of **1**, except

Table. *^{1}H- and ^{13}C-NMR Data* (500 and 125 MHz, resp.; CD_3OD) *of Compounds* **1** *and* **2**. δ in ppm, J in Hz. Trivial atom numbering as indicated in *Fig. 1*.

Position	**1**		**2**	
	δ(H)	δ(C)	δ(H)	δ(C)
1	5.05 (*d*, J = 3.8)	99.2	4.98 (*d*, J = 3.8)	99.3
3	4.83 (*dd*, J = 6.1, 2.5)	96.3	4.77 (*dd*, J = 6.2, 2.6)	96.3
4	1.97 – 1.98 (*m*, H_a), 1.92 – 1.93 (*m*, H_b)	30.2	1.83 – 1.84 (*m*, H_a), 1.92 – 1.93 (*m*, H_b)	30.2
5	2.32 – 2.34 (*m*)	34.0	2.31 – 2.33 (*m*)	34.0
6	5.26 (br. *d*, J = 8.3)	80.7	5.26 (*dd*, J = 8.3, 1.0)	81.0
7	3.65 (br. *s*)	61.4	3.61 (*d*, J = 1.0)	61.4
8	–	67.3	–	67.3
9	2.84 (*dd*, J = 8.2, 3.8)	41.2	2.79 (*dd*, J = 8.2, 3.8)	41.3
10	3.60, 4.08 (2*d*, J = 12.5)	61.2	3.53, 4.01 (2*d*, J = 12.8)	61.2
1′	–	127.6	–	121.8
2′	7.28 (*d*, J = 1.8)	111.8	7.88 (*d*, J = 8.8)	132.9
3′	–	149.5	6.82 (*d*, J = 8.8)	116.3
4′	–	151.0	–	164.0
5′	6.88 (*d*, J = 8.1)	116.5	6.82 (*d*, J = 8.8)	116.3
6′	7.16 (*dd*, J = 8.1, 1.8)	124.3	7.88 (*d*, J = 8.8)	132.9
7′	7.72 (*d*, J = 15.9)	147.4	–	168.3
8′	6.46 (*d*, J = 15.9)	115.0	–	–
9′	–	169.3	–	–
*Me*O–C(3′)	3.96 (*s*)	56.5	–	–
*Me*O–C(1)	3.51 (*s*)	55.2	3.45 (*s*)	55.2
*Me*O–C(3)	3.49 (*s*)	55.9	3.41 (*s*)	55.9

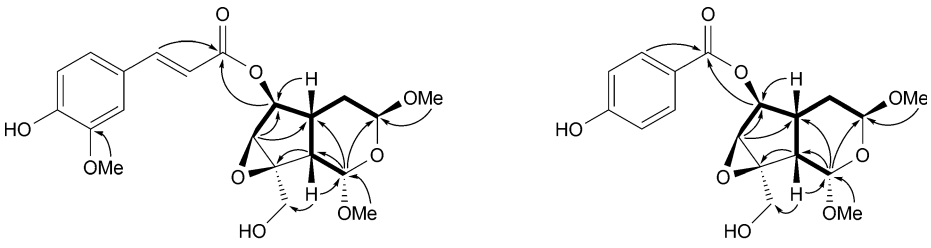

Fig. 2. *Key ^{1}H,^{1}H-COSY* (—) *and HMB* (H → C) *correlations of compounds* **1** *and* **2**

for the presence of signals for the 4-hydroxybenzoyl group (δ(H) 7.88 (*d*, J = 8.8, H–C(2′,6′)) and 6.82 (*d*, J = 8.8, H–C(3′,5′); δ(C) 121.8, 132.9 (C(2′,6′)), 116.3 (C(3′,5′)), 164.0, and 168.3 in **2**) instead of those of a (*E*)-feruloyl group **1** (*Table*). The HMBCs between H–C(6) signal (δ(H) 5.26) and C=O resonance (δ(C) 168.3) indicated that the 4-hydroxybenzoyl group was at C(6) (*Fig. 2*). The relative configuration of C_9-iridoid moiety of **2** was assumed to be same as that of **1** on the basis of their similar NOESY correlations (*Fig. 3*), *i.e.*, H–C(1)/H–C(9), H–C(1)/*Me*O–C(3), H–C(5)/H–C(9), H–C(5)/H_b–C(4), H–C(6)/H_a–C(4), and CH_2(10)/

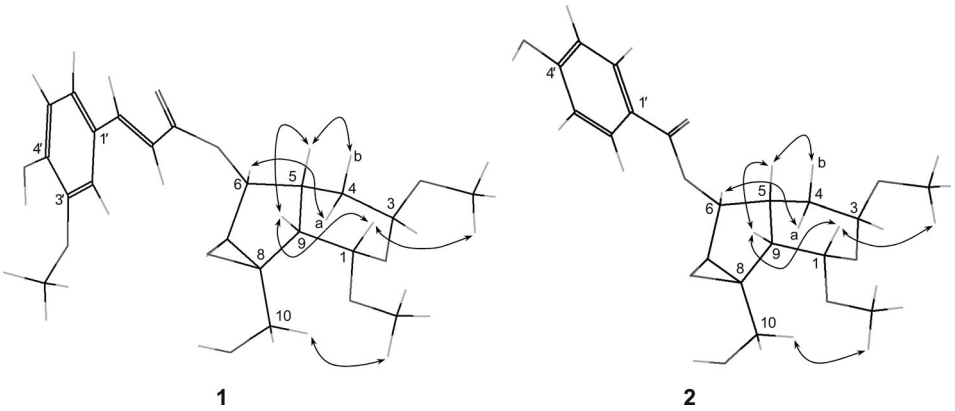

Fig. 3. *Key NOESY* (H ↔ H) *correlations of compounds* **1** *and* **2**

*Me*O–C(1). Accordingly, the structure of **2** was established as 6-*O*-(4-hydroxybenzoyl)jioglutin D.

In addition to the two new compounds described above, six known compounds, previously isolated from the genus *Catalpa*, were identified as minecoside (**3**) [14], specioside (**4**) [15], picroside II (**5**; 6-*O*-vanilloylcatalpol, amphicoside) [16][17], picroside III (**6**; 6-*O-trans*-feruloylcatalpol) [18], 4-hydroxybenzoic acid (**7**) [19], and martynoside (**8**) [20], by comparison of their spectroscopic data with those reported previously.

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Experimental Part

General. TLC: SiO_2 *60* F_{254} aluminum plates (*Merck*); detection under UV light and by spraying with 10% aq. H_2SO_4, followed by heating. Column chromatography (CC): silica gel (SiO_2; 70–230 mesh; *Merck*) and *Lichroprep* reversed-phase *RP-18* silica gel (40–63 μm; *Merck*). Prep. HPLC: *Waters 525* pump, *Waters 2996* detector; column *YMC J'sphere ODS-H80* column (150 × 20 mm i.d., 4 μm). Optical rotations: *Jasco DIP-1000* polarimeter. UV Spectra: *Jasco UV-550* spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *Jasco 4100* FT-IR spectrophotometer; KBr pellets; $\tilde{\nu}$ in cm^{-1}. ^1H-, ^{13}C-, and 2D-NMR spectra: *Bruker AMX-500* spectrometer; δ in ppm rel. to Me_4Si as internal standard; *J* in Hz. HR-ESI-MS: *Waters QTOF Micromass* spectrometer; in *m*/*z*.

Plant Material. The dried stem of *C. ovata* (Bignoniaceae) were collected from the herbal garden at the College of Pharmacy, Chungbuk National University, Korea, in October 2009, and identified by em. Prof. *Kyong Soon Lee* (College of Pharmacy, Chungbuk National University, Korea). A voucher specimen (CBNU 2009-CO-01) was deposited with the Herbarium of College of Pharmacy, Chungbuk National University, Korea.

Extraction and Isolation. The dried stem of *C. ovata* (1.0 kg) was extracted with MeOH three times at r.t. (3 × 3 l; overnight), and the soln. was evaporated *in vacuo*. The residue was suspended in H_2O (1 l), and then partitioned sequentially with hexane, AcOEt, and H_2O (each 3 × 1 l). The AcOEt-soluble fraction (10.2 g) was subjected to CC (SiO_2; CH_2Cl_2/MeOH 100:0 → 0:100): *Frs. COE1–COE4*. *Fr. COE2* (2.1 g) was further subjected to CC (*RP-18*; MeCN/H_2O 10:90 → 50:50): *Frs. COE2A*–

COE2C. *Fr. COE2A* (200 mg) was further purified by prep. HPLC (*YMC J'sphere ODS-H80*, MeCN/H_2O 45:65; 6 ml/min): **1** (t_R 17 min; 5 mg) and **2** (t_R 19 min; 4 mg). *Fr. COE2B* (600 mg) was separated by CC (SiO_2; CH_2Cl_2/MeOH 50:1 → 0:100): **3** (17 mg), **4** (3 mg), and **5** (10 mg). *Fr. COE2C* (700 mg) was further purified by prep. HPLC (*YMC J'sphere ODS-H80*, MeCN/H_2O 50:50, 6 ml/min): **6** (t_R 21 min; 21 mg), **7** (t_R 25 min; 10 mg), and **8** (t_R 18 min; 5 mg).

*6-*O*-[(*E*)-Feruloyl]jioglutin D* (=*(1aS,1bS,2S,4S,5aR,6S,6aS)-Octahydro-1a-(Hydroxymethyl)-2,4-dimethoxyoxireno[4,5]cyclopenta[1,2-c]pyran-6-yl (2E)-3-(4-Hydroxy-3-methoxyphenyl)prop-2-enoate*; **1**). White amorphous powder. $[\alpha]_D^{25} = -51.2$ ($c = 0.05$, MeOH). UV (MeOH): 215 (3.60), 228 (3.95), 310 (4.10). IR (KBr) 3405, 1710, 1635, 1450, 1390, 1265, 1175. ^{1}H- and ^{13}C-NMR (CD_3OD): see the *Table*. HR-ESI-MS: 445.1478 ($[M+Na]^+$, $C_{21}H_{26}NaO_9^+$; calc. 445.1475).

*6-*O*-(4-Hydroxybenzoyl)jioglutin D* (=*(1aS,1bS,2S,4S,5aR,6S,6aS)-Octahydro-1a-(Hydroxymethyl)-2,4-dimethoxyoxireno[4,5]cyclopenta[1,2-c]pyran-6-yl 4-Hydroxybenzoate*; **2**). White amorphous powder. $[\alpha]_D^{25} = -46.7$ ($c = 0.05$, MeOH). UV (MeOH): 218 (3.50), 264 (4.05), 292 (3.95). IR (KBr) 3500, 1708, 1610, 1525, 1263, 1015. ^{1}H- and ^{13}C-NMR (CD_3OD): see the *Table*. HR-ESI-MS: 389.1223 ($[M+Na]^+$, $C_{18}H_{22}NaO_8^+$; calc. 389.1212).

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