Studies on the Constituents of *Catalpa* Species. IX.[1] Iridoids from the Fallen Leaves of *Catalpa ovata* G. Don

Koichi Machida, Erika Hishinuma, and Masao Kikuchi*

Tohoku Pharmaceutical University; 4–4–1 Komatsushima, Aoba-ku, Sendai, Miyagi 981–8558, Japan.
Received December 10, 2003; accepted February 5, 2004

Two new iridoids, 6-*O*-*trans*-*p*-coumaroyl-7-deoxyrehmaglutin A (1) and 6-*O*-*cis*-*p*-coumaroyl-7-deoxyrehmaglutin A (2), were isolated from the fallen leaves of *Catalpa ovata* G. Don. together with six artifact iridoids (3—8). Their structures were established by spectral analysis. In addition, the scavenging effects of the principal compounds isolated from this plant on 1,1-diphenyl-2-picrylhydrazyl radical-scavenging activity were examined.

Key words *Catalpa ovata*; Bignoniaceae; fallen leaf; iridoid; radical-scavenging activity

Our previous phytochemical studies of Catalpae Fructus (kisasage in Japanese, Bignoniaceae) led to the isolation of 16 new iridoids.[2—5] In the course of further studies on the constituents of this plant, we studied the fresh and fallen leaves of *Catalpa ovata* G. Don, of which one constituent, *p*-hydroxybenzoic acid, has been identified.[6] The leaves of this plant have been used for the treatment of burns and athlete's foot, and the extract shows antibacterial activity.[7,8] We have recently reported the isolation of 10 new constituents from the $CHCl_3$ and AcOEt extracts of the fallen leaves of *C. ovata*.[1,9—11] In the present study, two new iridoids (**1**, **2**) and six artifact iridoids (**3**—**8**), were isolated from the remaining fraction. This paper deals with the structural elucidation and identification of these compounds. Additionally, we describe the radical-scavenging activity of the principal compounds isolated from this plant. The isolation procedure is described in detail in the Experimental section.

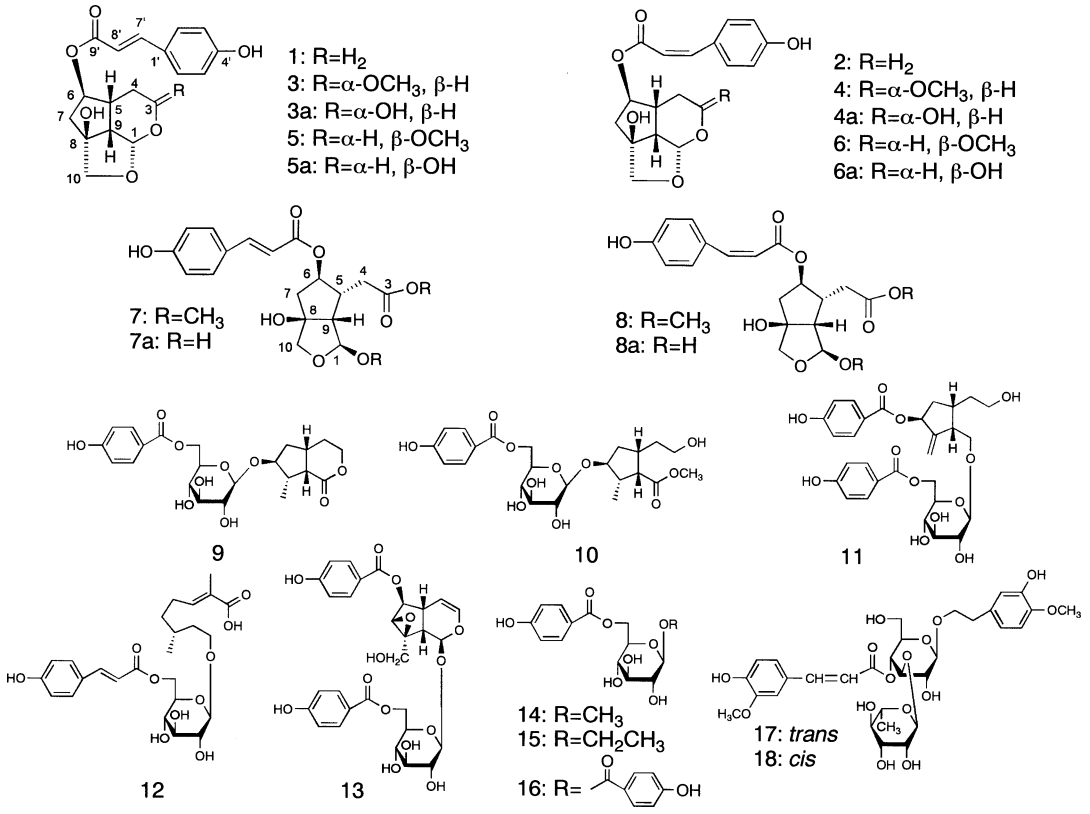
Compound **1** was obtained as an amorphous powder, $[\alpha]_D^{26}$ −17.7° (MeOH). The molecular formula of **1**, $C_{18}H_{20}O_6$, was confirmed by HR-FAB-MS. In the ^{1}H- and ^{13}C-NMR spectra of **1**, signal patterns were similar to those of des-*p*-hydroxybenzoyl-3-deoxycatalpin isolated from Catalpae Fructus,[5] except for the presence of a *trans*-*p*-coumaroyl group [δ_H 7.62 (1H, d, J=16.1 Hz, H-7′), 7.46 (2H, d, J=8.5 Hz, H-2′, 6′), 6.80 (2H, d, J=8.5 Hz, H-3′, 5′), 6.32 (1H, d, J=16.1 Hz, H-8′). δ_C 169.2 (s, C-9′)]. The NMR chemical shifts at the C-6 position of **1** were shifted downfield by 1.21 ppm (H-6) and 2.20 ppm (C-6) compared with those of des-*p*-hydroxybenzoyl-3-deoxycatalpin, suggesting that the *trans*-*p*-coumaroyl group is located at the C-6 hydroxyl group. This finding was supported by the heteronuclear multiple-bond connectivity (HMBC) correlation from H-6 to δ_C 169.2 (C-9′). The W-coupling between H-7β [δ_H 2.01 (1H, ddd, J=12.0, 10.3, 2.0 Hz)] and H-10β [δ_H 3.63 (1H, dd, J=9.8, 2.0 Hz)] and nuclear Overhauser enhancement spectroscopy (NOESY) correlation between 7-Hα [δ_H 2.46 (1H, dd, J=12.0, 6.1 Hz)] and H-6 [δ_H 5.23 (1H, ddd, J=10.3, 10.3, 6.1 Hz)] indicated that the configuration at C-6 of **1** was compatible with that of des-*p*-hydroxybenzoyl-3-deoxycatalpin. All other NOE correlations (H-1/H-9, H-3α/H-6, H-5/H-9) of **1** were the same those of des-*p*-hydroxybenzoyl-3-deoxycatalpin. Consequently, the structure of **1** was elucidated as shown and termed 6-*O*-*trans*-*p*-coumaroyl-7-deoxyrehmaglutin A.[12]

Compound **2** was obtained as an amorphous powder, $[\alpha]_D^{26}$ −15.4° (MeOH). The molecular formula of **2**, $C_{18}H_{20}O_6$, was confirmed by HR-FAB-MS and was coincident with that of **1**. Its ^{1}H-NMR spectrum closely resembled that of **1**, except that the olefin proton signals at δ_H 6.88 (H-7′) and 5.77 (H-8′) shifted upfield and their coupling constant (J=12.7 Hz) was smaller than that of **1**. This indicates that the configuration of the olefin in the *p*-coumaroyl moiety of **2** is in the *cis*-form. The ^{13}C-NMR spectrum confirmed that **2** is the *cis*-isomer of **1**. Consequently, the structure of **2** was elucidated as shown and termed 6-*O*-*cis*-*p*-coumaroyl-7-deoxyrehmaglutin A.

Compounds **3** and **4** were obtained as an amorphous powder, $[\alpha]_D^{26}$ −90.9° and −47.6° (MeOH), respectively. The ^{1}H- and ^{13}C-NMR spectra of **3** and **4** lacked the signal due to an oxymethylene group (C-3) of **1** and **2** and instead showed signals characteristic of a methoxyl [**3**, **4**: δ_H 3.40 (3H, s), δ_C 55.8] and an acetal methane [**3**: δ_H 4.70 (1H, t, J=4.4 Hz), δ_C 98.8. **4**: δ_H 4.69 (1H, t, J=4.4 Hz), δ_C 98.8] group, respectively. Furthermore, the ^{1}H-NMR signals of the acetal methane proton in both **3** and **4** are evidently coupled with H_2-4. The location of the methoxyl groups on C-3 in **3** and **4** was deduced from the HMBC correlation between the acetal methane proton (H-3) and the methoxyl carbon, respectively. On the other hand, the NOE interactions of both **3** and **4** were observed between H-1/H-3, H-3/Hβ-4, and Hβ-4/H-5. The above information indicates that both C-3 methoxyl groups have a α-quasiequatorial orientation with respect to the half-chair form of the tetrahydropyran ring. Consequently, the structures of **3** and **4** were elucidated as shown and termed 6-*O*-*trans*- and 6-*O*-*cis*-*p*-coumaroyl-3α-*O*-methyl-7-deoxyrehmaglutins A, respectively.

Compounds **5** and **6** were obtained as an amorphous powder, $[\alpha]_D^{26}$ −16.1° and +20.0° (MeOH), respectively. In the ^{1}H- and ^{13}C-NMR spectra of **5** and **6**, signal patterns were very similar to those of **3** and **4**, except for the difference chemical shifts of H-3, respectively. Comparison of the ^{1}H-NMR spectra of **5** and **3** and **6** and **4** showed a downfield shift of H-3 (0.26 ppm, respectively). There are also HMBC correlations between the H-3 and the methoxyl carbons of **5** and **6**. On the other hand, NOE interactions of both **5** and **6** were observed between H-3/H-6, H-3/Hα-4, and Hβ-4/H-5. The above information indicates that both C-3 methoxyl groups have a β-quasiequatorial orientation with respect to the half-chair form of the tetrahydropyran ring, and compounds **5** and **6** were revealed to be the epimers at C-3 of **3**

* To whom correspondence should be addressed. e-mail: mkikuchi@tohoku-pharm.ac.jp



and **4**, respectively. Consequently, the structures of **5** and **6** were elucidated as shown and termed 6-*O*-*trans*- and 6-*O*-*cis*-*p*-coumaroyl-3β-*O*-methyl-7-deoxyrehmaglutins A, respectively.

The configurational change of the methoxyl group at C-3 (**3** *vs.* **5**, **4** *vs.* **6**) introduces a considerable modification of the half-chair of the tetrahydropyran ring conformation, causing important NMR chemical shift changes in the ring carbons. The comparison of the ^{13}C-NMR chemical shifts of compounds **3** and **4** with those of **5** and **6** reveals shift changes at C-6 and C-9; the shielding of *ca.* 3.6 ppm of C-6 in **5** and **6** can be explained by the creation of a γ-gauche effect from C-3. On the other hand, the shielding of *ca.* 4 ppm of C-9 in **3** and **4** could be attributed to the γ-*syn* periplanar effect from C-3. That is, the considerable decrease in the C3—C-9 dihedral angle compared with **5** and **6** could explain the observed shielding of C-9 in **3** and **4**.

Compounds **7** and **8** were obtained as an amorphous powder, $[\alpha]_D^{26}$ $-12.5°$ and $+27.4°$ (MeOH), respectively. Both of the molecular formulas of **7** and **8** were determined to be $C_{20}H_{24}O_8$ by HR-FAB-MS. The NMR spectra of **7** and **8** exhibited signal patterns similar to those of **1** and **2**, although they lacked signals from the C-3 oxymethylene group of **1** and **2** and instead showed signals characteristic of the carbomethoxyl [**7**: δ_H 3.65 (3H, s), δ_C 52.3, 174.3. **8**: δ_H 3.64 (3H, s), δ_C 52.3, 174.2] and alcoholic methoxyl [**7**: δ_H 3.32 (3H, s), δ_C 55.0. **8**: δ_H 3.30 (3H, s), δ_C 55.0] groups, respectively. Both of the molecular formulas of **7** and **8** required 9 degrees of unsaturation. The *p*-coumaroyl and carbomethoxyl units have 7 degrees of unsaturation, and therefore **7** and **8** must have a two-ring system of the cyclopentane and furan rings in the skeleton itself, respectively. The gross structures of **7** and **8** were confirmed by HMBC [**7**: δ_H 3.32/C-1, δ_H 3.65, H_2-4/δ_C 174.3. **8**: δ_H 3.30/C-1, δ_H 3.64, H_2-4/δ_C 174.2] and NOESY [**7**, **8**: H-1/H-4a, H-10β/1-OCH_3] spectra. Consequently, the structures of **7** and **8** were elucidated as shown and termed 6-*O*-*trans*- and 6-*O*-*cis*-*p*-coumaroyl-1β-*O*-methylovatofuranic acid methyl esters, respectively.

Compounds **3**—**8** might be artifacts derived from new iridoids 6-*O*-*trans*- and 6-*O*-*cis*-*p*-coumaroyl-3α-hydroxy-7-deoxyrehmaglutins A (**3a**, **4a**), 6-*O*-*trans*- and 6-*O*-*cis*-*p*-coumaroyl-3β-hydroxy-7-deoxyrehmaglutins A (**5a**, **6a**), and 6-*O*-*trans*- and 6-*O*-*cis*-*p*-coumaroyl-1β-hydroxyovatofuranic acids (**7a**, **8a**), respectively, during the extraction and/or isolation process. We have already reported the coexistence of C-3 epimeric pairs of similar tricyclic iridoid derivatives such as catalpin (3β-OH) and epicatalpin (3α-OH)] in Catalpae Fructus.[2,4] Therefore there is a possibility that at least **3**—**6** are derived from **3a**—**6a** by recyclization of a tetrahydropyran ring in MeOH, respectively.

The 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical-scavenging activities of the above compounds (**1**—**8**) and principal glycosides (**9**—**18**)[10,11] isolated from the AcOEt fraction from this plant were investigated. Among them, Martynoside[11,13,14] (**17**, Reducing %: 40.0%) and 2-(3-hydroxy-4-methoxyphenyl) ethyl *O*-α-L-rhamnopyranosyl-(1$\rightarrow$3)-(4-*O*-*cis*-feruloyl)-β-D-glucopyranoside[11,15] (**18**, Reducing %: 29.8%) showed potent activities at 2.0×10^{-5} M comparable to that of *dl*-α-tocopherol (Reducing %: 40.0%), while the others with *p*-hydroxybenzoyl and/or *p*-coumaroyl groups were found to be almost inactive at 2.0×10^{-5} M.[16]

Experimental

General Experimental Procedures The instruments, experimental conditions, and plant material were the same as those described in the previous paper.[10]

Table 1. ^{1}H-NMR Chemical Shifts (CD_3OD)

Hydrogen	**1**[a]	**2**[a]	**3**[a]	**4**[a]	**5**[a]	**6**[a]	**7**[b]	**8**[b]
1	5.28 d (5.4)	5.26 d (5.6)	5.47 d (6.1)	5.45 d (6.3)	5.43 d (4.9)	5.42 d (5.1)	*ca.* 4.8	*ca.* 4.8
3α	3.95 m	3.94 m	—	—	4.96 dd (7.1, 5.6)	4.95 dd (7.1, 5.6)	—	—
3β	3.54 ddd (11.7, 5.1, 2.0)	3.54 ddd (11.7, 5.4, 1.7)	4.70 t (4.4)	4.69 t (4.4)	—	—	—	—
4α	1.54 br dd (14.1, 2.5)	1.48 br dd (14.4, 1.7)	1.69 dt (14.4, 4.4)	1.67 dt (14.4, 4.4)	1.97 ddd (14.4, 5.6, 2.9)	1.93 ddd (14.7, 5.6, 2.7)	2.58 dd (16.1, 6.2)	2.50 m
4β	1.81 m	1.76 m	1.87 m	1.81 m	1.54 ddd (14.4, 7.1, 4.9)	1.50 ddd (14.7, 7.1, 4.8)	2.48 dd (16.1, 9.2)	2.43 m
5	2.53 m	2.43 m	2.56 m	2.48 m	2.56 m	2.50 m	2.86 m	2.75 m
6	5.23 ddd (10.3, 10.3, 6.1)	5.15 ddd (10.5, 10.5, 6.1)	5.28 br dd (7.8, 6.1)	5.24 ddd (7.8, 6.1, 5.9)	5.13 ddd (9.8, 8.3, 6.3)	5.06 ddd (10.0, 8.5, 6.3)	4.79 ddd (10.3, 10.3, 7.0)	4.72 ddd (10.3, 10.3, 7.0)
7α	2.46 dd (12.0, 6.1)	2.43 m	2.47 dd (13.2, 5.9)	2.48 m	2.44 dd (12.7, 6.3)	2.43 dd (12.7, 6.3)	2.50 dd (13.6, 7.0)	2.50 m
7β	2.01 ddd (12.0, 10.3, 2.0)	1.94 ddd (12.0, 10.5, 2.0)	1.88 dd (13.2, 7.8)	1.81 m	1.91 dd (12.7, 9.8)	1.82 dd (12.7, 10.0)	1.90 ddd (13.6, 10.3, 1.5)	1.86 br dd (11.7, 10.3)
9	2.30 dd (10.2, 5.4)	2.25 dd (10.2, 5.6)	2.56 m	2.48 m	2.56 m	2.50 m	2.49 m	2.43 m
10α	3.95 d (9.8)	3.94 d (9.8)	3.89 d (9.5)	3.86 d (9.5)	3.86 br s	3.85 br s	3.77 d (8.8)	3.76 d (8.8)
10β	3.63 dd (9.8, 2.0)	3.63 dd (9.8, 2.0)	3.70 dd (9.5, 2.0)	3.69 dd (9.5, 2.0)			3.86 dd (8.8, 1.5)	3.85 dd (8.8, 1.5)
OCH_3	—	—	3.40 s	3.40 s	3.41 s	3.41 s	3.32 s	3.30 s
$COOCH_3$	—	—	—	—	—	—	3.65 s	3.64 s
2′, 6′	7.46 d (8.5)	7.59 d (8.6)	7.46 d (8.5)	7.59 d (8.5)	7.46 d (8.5)	7.59 d (8.5)	7.46 d (8.8)	7.61 d (8.8)
3′, 5′	6.80 d (8.5)	6.75 d (8.6)	6.80 d (8.5)	6.75 d (8.5)	6.80 d (8.5)	6.75 d (8.5)	6.80 d (8.8)	6.75 d (8.8)
7′	7.62 d (16.1)	6.88 d (12.7)	7.62 d (16.1)	6.86 d (12.7)	7.63 d (15.9)	6.89 d (12.9)	7.61 d (16.1)	6.89 d (12.8)
8′	6.32 d (16.1)	5.77 d (12.7)	6.33 d (16.1)	5.77 d (12.7)	6.33 d (15.9)	5.78 d (12.9)	6.30 d (16.1)	5.74 d (12.8)

Coupling constants (J in Hz) are given in parentheses. *a*) Measured at 400 MHz. *b*) Measured at 600 MHz. *ca.*, *circa*; br, broad.

Extraction and Isolation The extraction and isolation procedures were the same as those described in the previous paper.[10] The AcOEt-soluble fraction was chromatographed on a silica gel column ($CHCl_3$–MeOH–H_2O, 30 : 10 : 1) and the eluate was separated into 6 fractions (fr. 1—6). Fraction 2 was subjected to preparatory HPLC [column, Cosmosil 5C18-AR (10 mm i.d.×25 cm, Nacalai Tesque); mobile phase, MeOH–H_2O (2 : 3); UV detector, 314 nm; flow rate, 1.5 ml/min; column temperature, 35 °C] to give crude compounds, which were purified by preparatory HPLC [column, ODS-80TM (4.6 mm i.d.×15 cm, TOSOH); mobile phase, MeOH–H_2O (2 : 3); UV detector, 314 nm; flow rate, 1.5 ml/min; column temperature, 40 °C] to give **1** (25.0 mg), **2** (27.5 mg), **3** (12.5 mg), **4** (10.0 mg), **5** (15.0 mg), **6** (12.5 mg), **7** (8.5 mg), and **8** (5.7 mg), respectively. For these compounds, purification and instrumental analysis were carried out to avoid the effects of daylight.[17]

6-*O*-*trans*-*p*-Coumaroyl-7-deoxyrehmaglutin A (**1**): Amorphous powder. $[\alpha]_D^{26}$ −17.7° (c=0.2, MeOH). UV λ_{max} (MeOH) nm (log ε): 313 (4.25), 227 (3.94), 210 (3.93). FAB-MS *m*/*z*: 333 $(M+H)^+$, 355 $(M+Na)^+$. HR-FAB-MS *m*/*z*: 333.1338 (Calcd for $C_{18}H_{21}O_6$: 333.1338). ^{1}H-NMR (400 MHz, CD_3OD): Table 1. ^{13}C-NMR (100 MHz, CD_3OD): Table 2.

6-*O*-*cis*-*p*-Coumaroyl-7-deoxyrehmaglutin A (**2**): Amorphous powder. $[\alpha]_D^{26}$ −15.4° (c=0.2, MeOH). UV λ_{max} (MeOH) nm (log ε): 310 (4.06), 225 (3.95), 209 (3.95). FAB-MS *m*/*z*: 355 $(M+Na)^+$. HR-FAB-MS *m*/*z*: 355.1165 (Calcd for $C_{18}H_{20}O_6Na$: 355.1157). ^{1}H-NMR (400 MHz, CD_3OD): Table 1. ^{13}C-NMR (100 MHz, CD_3OD): Table 2.

6-*O*-*trans*-*p*-Coumaroyl-3α-*O*-methyl-7-deoxyrehmaglutin A (**3**): Amorphous powder. $[\alpha]_D^{26}$ −90.9° (c=0.1, MeOH). UV λ_{max} (MeOH) nm (log ε): 312 (4.24), 226 (3.94), 210 (3.91). FAB-MS *m*/*z*: 363 $(M+H)^+$, 385 $(M+Na)^+$. HR-FAB-MS *m*/*z*: 385.1253 (Calcd for $C_{19}H_{22}O_7Na$: 385.1263). ^{1}H-NMR (400 MHz, CD_3OD): Table 1. ^{13}C-NMR (100 MHz, CD_3OD): Table 2.

6-*O*-*cis*-*p*-Coumaroyl-3α-*O*-methyl-7-deoxyrehmaglutin A (**4**): Amorphous powder. $[\alpha]_D^{26}$ −47.6° (c=0.1, MeOH). UV λ_{max} (MeOH) nm (log ε): 308 (3.93), 225 (3.79), 210 (3.87). FAB-MS *m*/*z*: 363 $(M+H)^+$, 385 $(M+Na)^+$. HR-FAB-MS *m*/*z*: 385.1261 (Calcd for $C_{19}H_{22}O_7Na$: 385.1263). ^{1}H-NMR (400 MHz, CD_3OD): Table 1. ^{13}C-NMR (100 MHz, CD_3OD): Table 2.

Table 2. ^{13}C-NMR Chemical Shifts (CD_3OD)

Carbon	**1**[a]	**2**[a]	**3**[a]	**4**[a]	**5**[a]	**6**[a]	**7**[b]	**8**[b]
1	101.6	101.6	101.4	101.4	100.0	100.0	107.1	107.1
3	57.1	57.0	98.8	98.8	98.7	98.6	174.3	174.2
4	22.9	22.8	28.2	28.1	28.2	28.1	34.5	34.4
5	39.4	39.2	38.4	38.1	40.4	40.2	43.0	42.8
6	74.5	74.3	80.9	80.5	77.2	77.0	77.3	77.1
7	46.3	46.2	43.9	43.7	44.2	44.1	46.6	46.4
8	84.4	84.3	87.9	87.7	85.6	85.5	84.6	84.5
9	47.7	47.5	50.1	49.8	54.0	53.9	58.5	58.4
10	78.5	78.5	78.3	78.3	79.4	79.8	78.2	78.3
OCH_3	—	—	55.8	55.8	55.9	55.9	55.0	55.0
$COOCH_3$	—	—	—	—	—	—	52.3	52.3
1′	127.1	127.7	127.2	127.8	127.2	127.8	127.0	127.7
2′, 6′	131.3	133.6	131.2	133.5	131.3	133.6	131.3	133.7
3′, 5′	116.9	115.9	116.9	115.9	116.9	115.9	117.0	115.9
4′	161.6	160.3	161.4	160.1	161.5	160.2	162.1	160.9
7′	146.9	145.2	146.7	144.8	147.0	145.3	147.1	145.6
8′	114.9	116.7	115.3	117.0	115.0	116.7	114.7	116.9
9′	169.2	168.3	169.1	168.2	169.1	168.2	168.8	167.9

a) Measured at 100 MHz. *b*) Measured at 150 MHz.

6-*O*-*trans*-*p*-Coumaroyl-3β-*O*-methyl-7-deoxyrehmaglutin A (**5**): Amorphous powder. $[\alpha]_D^{26}$ −16.1° (c=0.3, MeOH). UV λ_{max} (MeOH) nm (log ε): 312 (4.36), 226 (4.05), 210 (4.02). FAB-MS *m*/*z*: 385 $(M+Na)^+$. HR-FAB-MS *m*/*z*: 415.1303 (Calcd for $C_{19}H_{22}O_7Na$: 385.1263). ^{1}H-NMR (400 MHz,

CD_3OD): Table 1. ^{13}C-NMR (100 MHz, CD_3OD): Table 2.

6-*O*-*cis*-*p*-Coumaroyl-3β-*O*-methyl-7-deoxyrehmaglutin A (**6**): Amorphous powder. $[\alpha]_D^{26}$ +20.0° (c=0.3, MeOH). UV λ_{max} (MeOH) nm (log ε): 309 (4.10), 225 (3.94), 210 (4.02). FAB-MS m/z: 385 $(M+Na)^+$. HR-FAB-MS m/z: 385.1243 (Calcd for $C_{19}H_{22}O_7Na$: 385.1263). ^1H-NMR (400 MHz, CD_3OD): Table 1. ^{13}C-NMR (100 MHz, CD_3OD): Table 2.

6-*O*-*trans*-*p*-Coumaroyl-1β-*O*-methylovatofuranic acid methyl ester (**7**): Amorphous powder. $[\alpha]_D^{26}$ −12.5° (c=0.1, MeOH). UV λ_{max} (MeOH) nm (log ε): 311 (4.44), 225 (4.14), 210 (4.13). FAB-MS m/z: 415 $(M+Na)^+$. HR-FAB-MS m/z: 415.1406 (Calcd for $C_{20}H_{24}O_8Na$: 415.1369). ^1H-NMR (600 MHz, CD_3OD): Table 1. ^{13}C-NMR (150 MHz, CD_3OD): Table 2.

6-*O*-*cis*-*p*-Coumaroyl-1β-*O*-methylovatofuranic acid methyl ester (**8**): Amorphous powder. $[\alpha]_D^{26}$ +27.4° (c=0.1, MeOH). UV λ_{max} (MeOH) nm (log ε): 311 (4.00), 225 (3.79), 211 (3.86). FAB-MS m/z: 415 $(M+Na)^+$. HR-FAB-MS m/z: 415.1406 (Calcd for $C_{20}H_{24}O_8Na$: 415.1369). ^1H-NMR (600 MHz, CD_3OD): Table 1. ^{13}C-NMR (150 MHz, CD_3OD): Table 2.

Measurement of DPPH Radical-Scavenging Activity[18] MeOH solutions of compounds **1**—**8** and the principal glycosides[10,11] isolated from the AcOEt fraction of this plant (4×10^{-5} M, 1.0 ml) were each added to 0.5 mM DPPH/MeOH solution (1.0 ml), and the absorbance of each mixture was determined at 517 nm after 30 min. The radical-scavenging activity was determined by comparing the absorbance with that of the blank (100%) containing only DPPH and solvent. *dl*-α-Tocopherol was used as a standard, and measurement was done in triplicate. % reduction=$100\times[(Abs_{blank}-Abs_{sample})/Abs_{blank}]$.

Acknowledgments The authors are grateful to Mrs. S. Sato and T. Tatsuki of their university for NMR and MS measurements.

References and Notes

1) Part 9 in the series "Studies on the Constituents of *Catalpa* Species." For part 8: Machida K., Shioda K., Yaoita Y., Kakuda R., Kikuchi M., *Nat. Med.*, **55**, 147—148 (2001).
2) Kanai E., Machida K., Kikuchi M., *Chem. Pharm. Bull.*, **44**, 1607—1609 (1996).
3) Machida K., Ogawa M., Kikuchi M., *Chem. Pharm. Bull.*, **46**, 1056—1057 (1998).
4) Ikeda C., Machida K., Kakuda R., Yaoita Y., Kikuchi M., *J. Tohoku Pharm. Univ.*, **46**, 63—69 (1999).
5) Machida K., Ikeda C., Kakuda R., Yaoita Y., Kikuchi M., *Nat. Med.*, **55**, 61—63 (2001).
6) Nakaoki T., Morita N., *Yakugaku Zasshi*, **75**, 171—172 (1955).
7) Shanghai Scientific Technological Publishers and Shougakukan (eds.), "Dictionary of Chinese Materia Medica," Shougakukan, Tokyo, 1985, p. 1196.
8) Tanioka R., *Yamaguchi Igaku*, **10**, 1178—1180 (1961).
9) Shioda K., Machida K., Kakuda R., Yaoita Y., Kikuchi M., *J. Tohoku Pharm. Univ.*, **47**, 61—65 (2000).
10) Machida K., Ando M., Yaoita Y., Kakuda R., Kikuchi M., *Chem. Pharm. Bull.*, **49**, 732—736 (2001).
11) Machida K., Ando M., Yaoita Y., Kakuda R., Kikuchi M., *Nat. Med.*, **55**, 64—67 (2001).
12) des-*p*-hydroxybenzoyl-3-deoxycatalpin=7-deoxyrehmaglutin A rehmaglutin A: Kitagawa I., Fukuda Y., Taniyama T., Yoshikawa M., *Chem. Pharm. Bull.*, **34**, 1399—1402 (1986).
13) Sasaki H., Taguchi H., Endo T., Yoshioka I., Higashiyama K., Otomatsu H., *Chem. Pharm. Bull.*, **26**, 2111—2121 (1978).
14) Miyase T., Koizumi A., Ueno A., Noro T., Kuroyanagi M., Fukushima S., Akiyama Y., Takemoto T., *Chem. Pharm. Bull.*, **30**, 2732—2737 (1982).
15) Matsuura Y., Miyaichi Y., Tomimori T., *Yakugaku Zasshi*, **114**, 775—788 (1994).
16) Reducing %: **1** (1.5%), **2** (1.5%), **3** (5.5%), **4** (4.0%), **5** (6.2%), **6** (5.4%), **7** (10.5%), **8** (7.2%), ovatolactone 7-*O*-(6′-*O*-*p*-hydroxybenzoyl)-β-D-glucopyranoside (**9**, 7.0%), ovatic acid methyl ester 7-*O*-(6′-*O*-*p*-hydroxybenzoyl)-β-D-glucopyranoside (**10**, 6.4%), 7-*O*-*p*-hydroxybenzoylovatol 1-*O*-(6′-*O*-*p*-hydroxybenzoyl)-β-D-glucopyranoside (**11**, 9.5%), (2*E*,6*R*)-2,6-dimethyl-8-hydroxy-2-octenoic acid 8-*O*-[6′-*O*-(*E*)-*p*-coumaroyl]-β-D-glucopyranoside (**12**, 5.3%), 6′-*O*-*p*-hydroxybenzoyl catalposide (**13**, 5.3%), methyl (6-*O*-*p*-hydroxybenzoyl)-β-D-glucopyranoside (**14**, 8.3%), ethyl (6-*O*-*p*-hydroxybenzoyl)-β-D-glucopyranoside (**15**, 7.6%), 1,6-di-*O*-*p*-hydroxybenzoyl-β-D-glucopyranoside (**16**, 7.9%).
17) Machida K., Kikuchi M., *Chem. Pharm. Bull.*, **41**, 248—251 (1993).
18) Blois M. S., *Nature* (London), **181**, 1199—1200 (1958).