

## Isolation of Flavonoids and a Cerebroside from the Stem Bark of *Albizzia julibrissin*

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(Received April 19, 2004)

From the EtOAc fraction of the MeOH extract of *Albizzia julibrissin* (Leguminosae), a rare 5-deoxyflavone (geraldone, **1**), isookanin (**2**), luteolin (**3**), an isoflavone (daidzein, **4**), five prenylated flavonoids [sophoflavescenol (**5**), kurarinone (**6**), kurarinol (**7**), kuraridin (**8**) and kuraridinol (**9**)], a cerebroside (soya-cerebroside I, **10**), and (-)-syringaresinol-4-O- $\beta$ -D-glucopyranoside (**11**) were isolated and characterized on the basis of spectral data. Compounds **2**, **3**, and **11**, showed 1,1-diphenyl-2-picrylhydrazyl radical scavenging activity.

**Key words:** *Albizzia julibrissin*, Geraldone, Isookanin, Soya-cerebroside I, 1,1-Diphenyl-2-picrylhydrazyl (DPPH) radicals

### INTRODUCTION

The dried stem bark of *Albizzia julibrissin* Durazz (Leguminosae) has been used to treat insomnia, diuresis, sthenia, ascaricide, and contusion in China, Japan, and Korea (Kim, 1996). In a previous study, we reported the antioxidative effect of *A. julibrissin* and active components such as sulfuretin and 3',4',7-trihydroxyflavone isolated from the EtOAc soluble fraction of this plant (Jung *et al.*, 2003). In our continuous study on this plant, we isolated geraldone (**1**), isookanin (**2**), luteolin (**3**), daidzein (**4**), five prenylated flavonoids [sophoflavescenol (**5**), kurarinone (**6**), kurarinol (**7**), kuraridin (**8**), and kuraridinol (**9**)], soya-cerebroside I (**10**), and (-)-syringaresinol-4-O- $\beta$ -D-glucopyranoside (**11**). The present paper describes the structural characterization and scavenging activity on DPPH radicals of these compounds.

### MATERIALS AND METHODS

#### General experimental procedures

The EI and GC mass data were recorded using a GC-MS QP-5050A spectrometer. The LR- and HR-FAB mass

data were recorded using JMS-HX110A/HX110A Tandem mass spectrometer (JEOL). Optical rotations were recorded on a Perkin-Elmer 341 polarimeter. The <sup>1</sup>H- and <sup>13</sup>C-NMR spectra were measured using a JEOL JNM-ECP 400 (400 MHz for <sup>1</sup>H, 100 MHz for <sup>13</sup>C) spectrometer. The chemical shifts were referenced to the respective residual solvent peaks ( $\delta_H$  3.30 and  $\delta_C$  49.0 for CD<sub>3</sub>OD,  $\delta_H$  2.50 and  $\delta_C$  39.5 for DMSO-*d*<sub>6</sub>, and  $\delta_H$  7.19, 7.55, and 8.17 and  $\delta_C$  123.5, 135.5, and 149.5 for pyridine-*d*<sub>5</sub>). The DEPT, HMQC, HMBC, and COSY spectra were recorded on a JEOL JNM-EPC 400 using pulsed field gradients. Column chromatography was carried out using Si gel (Merck, 70-230 mesh), Sephadex LH-20 (Sigma, 25-100  $\mu$ m), and RP-18 gel (Merck, 40-63  $\mu$ m). The TLC was performed on a precoated Merck Kieselgel 60 F<sub>254</sub> plate (0.25 mm) and a Merck RP-18 F<sub>254s</sub> plate (5 $\times$ 10 cm). 50% H<sub>2</sub>SO<sub>4</sub> was used as the spray reagent.

#### Chemicals

1,1-Diphenyl-2-picrylhydrazyl and L-ascorbic acid were purchased from Sigma Chemical Company (St. Louis, MO, USA).

#### Plant materials

The stem bark of *Albizzia julibrissin* Durazz (Leguminosae) was purchased from the herbal medicine co-operative association in Busan Province, in August 2001. A voucher

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specimen (no. 20010820) was deposited at the Faculty of Food Science and Biotechnology, Pukyong National University.

### Isolation of compounds 1-11

The stem bark (18.2 kg) of *A. julibrissin* was refluxed with MeOH for three hours (18 L $\times$ 3). The total filtrate was concentrated to dryness *in vacuo* at 40°C to render the MeOH extract (2.97 kg), and this extract was suspended in distilled water and partitioned with CH<sub>2</sub>Cl<sub>2</sub> (932 g), EtOAc (86 g), *n*-BuOH (650 g), and H<sub>2</sub>O (1182 g) in sequence. The EtOAc (86 g) fraction was chromatographed on a Si gel column using CH<sub>2</sub>Cl<sub>2</sub>-MeOH (gradient) to yield 29 subfractions. Fractions 14-18 (8.5 g) were separately purified by Sephadex LH-20, with MeOH, to obtain compounds **1** (18 mg), **4** (40 mg), **5** (7 mg), and **8** (6 mg). The fraction 19 (14.6 g) was further chromatographed on a Sephadex LH-20 and RP-18 gel column with H<sub>2</sub>O-MeOH (gradient) to give compounds **2** (20 mg), **3** (20 mg), and **6** (7 mg). Fraction 20 (17.5 g) was subjected to column chromatography over Sephadex LH-20 and RP-18, eluted with H<sub>2</sub>O-MeOH (gradient) to afford 10 subfractions. Fraction 20-1 (6.4 g) was chromatographed on the Si gel column with CH<sub>2</sub>Cl<sub>2</sub>-MeOH-H<sub>2</sub>O (12:1:0.1) to give compound **9** (10 mg). Fraction 20-4 (2.4 g) was further chromatographed on a Sephadex LH-20 and RP-18 gel column with H<sub>2</sub>O-MeOH (gradient) to obtain compounds **7** (16 mg), **10** (120 mg), and **11** (50 mg), respectively.

### Geraldone (1)

Amorphous yellow powder; UV  $\lambda_{\max}$  (MeOH) (log  $\epsilon$ ): 237 (4.16), 313 (sh. 4.04), 337 (4.14); +NaOMe : 254 (4.12), 319 (sh. 3.92), 3.70 (4.00); +AlCl<sub>3</sub> : 237 (4.15), 315 (sh. 4.04), 337 (4.13); +AlCl<sub>3</sub>+HCl : 236 (4.15), 315 (sh. 4.03), 337 (4.12), 408 (sh. 3.17); +NaOAc : 246 (4.11), 352 (4.08); +NaOAc+H<sub>3</sub>BO<sub>3</sub> : 236 (4.15), 315 (sh. 4.03), 338 (4.12) nm; C<sub>16</sub>H<sub>12</sub>O<sub>5</sub>; EIMS *m/z* (rel. int.)  $\delta$  : 284 ([M]<sup>+</sup>, 100), 256 ([M-CO]<sup>+</sup>, 23.0), 253 ([M-OMe]<sup>+</sup>, 7.3), 148 ([B<sub>1</sub>]<sup>+</sup>, 28.1), 137 ([A<sub>1</sub>+H]<sup>+</sup>, 54.8); <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  : 7.86 (1H, d, *J* = 8.6 Hz, H-5), 7.54 (1H, d, *J* = 2.2 Hz, H-2'), 7.54 (1H, dd, *J* = 8.9, 2.2 Hz, H-6'), 6.99 (1H, d, *J* = 2.2 Hz, H-8), 6.93 (1H, d, *J* = 9.0 Hz, H-5'), 6.90 (1H, dd, *J* = 8.7, 2.2 Hz, H-6), 6.83 (1H, s, H-3), 3.89 (3H, s, OCH<sub>3</sub>); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  : 176.3 (C-4), 162.6 (C-7), 162.3 (C-2), 157.4 (C-9), 150.2 (C-4'), 148.0 (C-3'), 126.4 (C-5), 122.1 (C-1'), 119.9 (C-6'), 116.1 (C-10), 115.7 (C-5'), 114.7 (C-6), 110.0 (C-2'), 104.8 (C-3), 102.5 (C-8), 55.9 (OCH<sub>3</sub>).

### Isookanin (2)

Amorphous orange powder;  $[\alpha]_D^{20}$  -2° (c 0.10, MeOH); UV  $\lambda_{\max}$  (MeOH) (log  $\epsilon$ ): 233 (sh. 4.24), 287 (4.13), 375 (3.75); +NaOMe : 253 (4.04), 291 (sh. 3.77), 337 (4.20),

437 (3.57); +AlCl<sub>3</sub> : 249 (3.99), 294 (sh. 3.71), 313 (3.83), 352 (sh. 3.19), 476 (2.77); +AlCl<sub>3</sub>+HCl : 232 (sh. 4.24), 285 (4.11), 424 (3.80); +NaOAc : 232 (sh. 4.22), 258 (4.13), 288 (4.05), 332 (3.99), 379 (3.77); +NaOAc+H<sub>3</sub>BO<sub>3</sub> : 243 (sh. 4.23), 297 (4.06), 308 (4.06), 396 (3.71) nm; <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$  : 7.29 (1H, d, *J* = 8.7 Hz, H-5), 6.98 (1H, d, *J* = 1.7 Hz, H-2'), 6.85 (1H, dd, *J* = 8.2, 1.7 Hz, H-6'), 6.78 (1H, d, *J* = 8.2 Hz, H-5'), 6.51 (1H, d, *J* = 8.7 Hz, H-6), 5.36 (1H, dd, *J* = 12.4, 3.0 Hz, H-2), 3.06 (1H, dd, *J* = 16.9, 12.4 Hz, H-3<sub>ax</sub>), 2.72 (1H, dd, *J* = 16.9, 3.0 Hz, H-3<sub>eq</sub>); <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>OD)  $\delta$  : 194.8 (C-4), 154.8 (C-7), 153.5 (C-9), 147.7 (C-4'), 147.3 (C-3'), 134.8 (C-8), 132.7 (C-1'), 120.4 (C-6'), 120.1 (C-5), 117.0 (C-5'), 116.5 (C-10), 115.8 (C-2'), 111.7 (C-6), 82.4 (C-2), 45.9 (C-3).

### Luteolin (3)

Amorphous yellow powder; UV  $\lambda_{\max}$  (MeOH) (log  $\epsilon$ ): 254 (4.20), 268 (sh. 4.16), 348 (4.24); +NaOMe : 230 (sh. 4.65), 266 (4.65), 328 (sh. 4.27), 403 (4.63); +AlCl<sub>3</sub> : 273 (4.29), 300 (sh. 3.90), 424 (4.35); +AlCl<sub>3</sub>+HCl : 267 (sh. 4.18), 275 (4.19), 294 (4.01), 360 (4.16), 390 (4.18); +NaOAc : 269 (4.22), 360 (4.14); +NaOAc+H<sub>3</sub>BO<sub>3</sub> : 260 (4.31), 371 (4.27) nm; <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  : 12.97 (1H, s, OH-5), 10.80 (1H, s, OH-7), 9.90 (1H, s, OH-4'), 9.39 (1H, s, OH-3'), 7.41 (1H, dd, *J* = 8.0, 2.0 Hz, H-6'), 7.39 (1H, d, *J* = 2.0 Hz, H-8), 6.88 (1H, d, *J* = 8.0 Hz, H-5'), 6.66 (1H, s, H-3), 6.43 (1H, d, *J* = 2.0 Hz, H-6), 6.18 (1H, d, *J* = 2.0 Hz, H-2'); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  : 181.6 (C-4), 164.1 (C-2), 163.9 (C-7), 161.5 (C-5), 157.3 (C-9), 149.7 (C-4'), 145.7 (C-3'), 121.5 (C-6'), 119.0 (C-1'), 116.0 (C-5'), 113.4 (C-2'), 103.7 (C-10), 102.9 (C-3), 98.8 (C-6), 93.8 (C-8).

### Daidzein (4)

Colorless needles; C<sub>15</sub>H<sub>8</sub>O<sub>4</sub>; EIMS *m/z* (rel. int.) : 254 ([M]<sup>+</sup>, 100), 137 ([A<sub>1</sub>+H]<sup>+</sup>, 56), 118 ([B<sub>1</sub>]<sup>+</sup>, 44); <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$  : 8.12 (1H, s, H-2), 8.05 (1H, d, *J* = 9.0 Hz, H-5), 7.36 (2H, d, *J* = 8.0 Hz, H-2', 6'), 6.93 (1H, dd, *J* = 8.0, 2.0 Hz, H-6), 6.84 (1H, d, *J* = 2.0 Hz, H-8), 6.83 (2H, d, *J* = 8.0 Hz, H-3', 5'); <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>OD)  $\delta$  : 179.0 (C-4), 165.5 (C-7), 160.6 (C-9), 159.5 (C-4'), 155.4 (C-2), 132.2 (C-2', C-6'), 129.3 (C-5), 126.8 (C-1'), 125.1 (C-3), 119.0 (C-10), 117.3 (C-6), 117.0 (C-3', C-5'), 104.0 (C-8).

### Sophoflavescenol (5)

Amorphous yellow powder; <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  : 10.58 (1H, s, OH-7), 9.99 (1H, s, OH-4'), 7.98 (2H, d, *J* = 8.8 Hz, H-2', 6'), 6.91 (2H, d, *J* = 8.8 Hz, H-3', 5'), 6.44 (1H, s, H-6), 5.18 (1H, t-like, H-2"), 3.80 (OCH<sub>3</sub>), 3.46 (2H, brd, *J* = 6.7 Hz, H-1"), 1.75 (3H, s, H-5"), 1.62 (3H, s, H-4"); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  : 171.2 (C-4), 159.5

(C-7), 158.5 (C-4'), 157.9 (C-5), 155.4 (C-9), 141.8 (C-2), 136.8 (C-3), 130.9 (C-3''), 128.6 (C-2', 6'), 122.7 (C-2''), 122.3 (C-1'), 115.4 (C-3', 5'), 106.8 (C-8), 105.2 (C-10), 95.4 (C-6), 55.7 (OCH<sub>3</sub>), 25.4 (C-4''), 21.5 (C-1''), 17.8 (C-5'').

#### Kurarinone (6)

Amorphous orange powder;  $[\alpha]_D^{20} +12^\circ$  (c 0.10, MeOH); <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  : 10.32 (1H, s, OH-7), 9.55 (1H, s, OH-2'), 9.30 (1H, s, OH-4'), 7.22 (1H, d, *J* = 8.4 Hz, H-6'), 6.33 (1H, d, *J* = 2.2 Hz, H-3'), 6.26 (1H, dd, *J* = 8.4, 2.2 Hz, H-5'), 6.12 (1H, s, H-6), 5.42 (1H, dd, *J* = 13.3, 2.4 Hz, H-2), 4.90 (1H, m, H-4''), 4.55 (1H, brs, H-9''), 4.48 (1H, d, *J* = 2.0 Hz, H-9''), 3.70 (3H, s, OCH<sub>3</sub>), 2.81 (1H, dd, *J* = 16.5, 13.2 Hz, H-3<sub>ax</sub>), 2.50 (2H, m, H-1''), 2.48 (1H, m, H-2''), 2.45 (1H, dd, *J* = 16.5, 2.5 Hz, H-3<sub>eq</sub>), 1.95 (2H, m, H-3''), 1.58 (3H, s, H-10''), 1.53 (3H, s, H-7''), 1.43 (3H, s, H-6''); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  : 188.9 (C-4), 162.4 (C-5), 162.0 (C-7), 159.6 (C-9), 158.1 (C-4'), 155.2 (C-2'), 147.9 (C-8''), 130.6 (C-5''), 127.2 (C-6'), 123.4 (C-4''), 116.3 (C-1'), 110.7 (C-9''), 106.9 (C-8), 106.2 (C-5'), 104.3 (C-10), 102.3 (C-3'), 92.4 (C-6), 73.5 (C-2), 55.2 (OCH<sub>3</sub>), 46.3 (C-2''), 44.3 (C-3), 30.7 (C-3''), 26.9 (C-1''), 25.5 (C-6''), 18.6 (C-10''), 17.5 (C-7'').

#### Kurarinol (7)

Colorless needles;  $[\alpha]_D^{20} -3^\circ$  (c 0.012, MeOH); UV  $\lambda_{\max}$  (MeOH) (log  $\epsilon$ ) : 223 (4.38), 287 (4.23), 317 (3.76), 386 (3.27); +NaOMe : 248 (4.03), 287 (3.79), 330 (4.39), 439 (3.37); +AlCl<sub>3</sub> : 224 (4.35), 286 (4.20), 318 (3.73), 338 (3.23); +AlCl<sub>3</sub>+HCl : 223 (4.35), 286 (4.19), 321 (3.69), 402 (3.19); +NaOAc : 222 (4.37), 287 (4.20), 324 (3.77), 389 (3.27); +NaOAc+H<sub>3</sub>BO<sub>3</sub> : 223 (4.38), 287 (4.21), 319 (3.75), 390 (3.25) nm; HR-FABMS : [M+H]<sup>+</sup> Found *m/z* 457.2223; calc for C<sub>26</sub>H<sub>33</sub>O<sub>7</sub> 457.2226; <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  : 7.21 (1H, d, *J* = 8.4 Hz, H-6'), 6.32 (1H, d, *J* = 2.3 Hz, H-3'), 6.25 (1H, dd, *J* = 8.4, 2.3 Hz, H-5'), 6.12 (1H, s, H-6), 5.41 (1H, dd, *J* = 13.2, 2.7 Hz, H-2), 4.56 and 4.48 (each 1H, brs, H-9''), 3.70 (3H, s, 5-OMe), 2.80 (1H, dd, *J* = 16.0, 13.2 Hz, H-3<sub>ax</sub>), 2.50 (1H, m, H-3<sub>eq</sub>), 2.49 (2H, m, H-1''), 2.30 (1H, m, H-2''), 1.56 (3H, s, H-10''), 1.23 (2H, m, H-3''), 1.00 (2H, m, H-4''), 0.95 (6H, s, H-6'', 7''); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  : 188.9 (C-4), 162.4 (C-9), 162.0 (C-7), 159.5 (C-5), 158.0 (C-4'), 155.2 (C-2'), 148.1 (C-8''), 127.2 (C-6'), 116.3 (C-1'), 110.8 (C-9''), 107.0 (C-8), 106.2 (C-5'), 104.3 (C-10), 102.3 (C-3'), 92.4 (C-6), 73.5 (C-2), 68.6 (C-5''), 55.2 (OCH<sub>3</sub>), 46.5 (C-2''), 41.4 (C-4''), 29.4 (C-6''), 28.9 (C-7''), 27.4 (C-1''), 26.4 (C-3''), 18.0 (C-10''); <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD)  $\delta$  : 7.29 (1H, d, *J* = 8.3 Hz, H-6'), 6.33 (1H, dd, *J* = 8.3, 2.3 Hz, H-5'), 6.32 (1H, d, *J* = 2.3 Hz, H-3'), 6.10 (1H, s, H-6), 5.53 (1H, dd, *J* = 13.0, 2.3 Hz, H-2), 4.60 and 4.53 (2H, dd, *J* = 2.4, 1.3 Hz, H-9''), 3.79 (3H, s, OCH<sub>3</sub>), 2.86 (1H,

dd, *J* = 16.0, 13.0 Hz, H-3<sub>ax</sub>), 2.69 (1H, dd, *J* = 16.0, 2.3 Hz, H-3<sub>eq</sub>), 2.62 (2H, d, *J* = 7.0 Hz, H-1''), 2.39 (1H, m, H-2''), 1.63 (3H, s, H-10''), 1.38 (2H, m, H-3''), 1.28 (2H, m, H-4''), 1.06 (3H, s, H-6''), 1.05 (3H, s, H-7''); <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>OD)  $\delta$  : 194.7 (C-4), 165.7 (C-8), 165.5 (C-9), 162.7 (C-5), 160.3 (C-4'), 157.4 (C-2'), 150.4 (C-8''), 129.3 (C-6'), 119.2 (C-1'), 112.4 (C-9''), 110.3 (C-7), 108.4 (C-5'), 106.6 (C-10), 104.2 (C-3'), 94.1 (C-6), 76.3 (C-2), 72.3 (C-5''), 56.7 (OCH<sub>3</sub>), 49.2 (C-2''), 46.4 (C-3), 43.6 (C-4''), 30.0 (C-6''), 29.7 (C-7''), 29.5 (C-1''), 28.9 (C-3''), 19.5 (C-10'').

#### Kuraridin (8)

Amorphous orange powder;  $[\alpha]_D^{20} +1.2^\circ$  (c 0.025, MeOH); UV  $\lambda_{\max}$  (MeOH) (log  $\epsilon$ ) : 289 (3.92), 369 (4.19); +NaOMe : 332 (4.20), 456 (4.34); +AlCl<sub>3</sub> : 292 (3.90), 390 (4.12); +AlCl<sub>3</sub>+HCl : 295 (3.84), 399 (4.07); +NaOAc : 291 (3.93), 386 (4.19); +NaOAc+H<sub>3</sub>BO<sub>3</sub> : 291 (3.93), 386 (4.19) nm; HR-FABMS : [M+H]<sup>+</sup> Found *m/z* 439.2121; calc for C<sub>26</sub>H<sub>31</sub>O<sub>6</sub> 439.2121; EIMS *m/z* (rel. int.)  $\delta$  : 438 ([M]<sup>+</sup>, 100), 315 ([M-C<sub>9</sub>H<sub>15</sub>]<sup>+</sup>, 20), 288 ([A<sub>1</sub>]<sup>+</sup>, 17), 165 ([A<sub>1</sub>-C<sub>9</sub>H<sub>15</sub>]<sup>+</sup>, 79), 150 ([B<sub>1</sub>]<sup>+</sup>, 17); <sup>1</sup>H-NMR (400 MHz, CD<sub>3</sub>OD) : 7.99 (1H, d, *J* = 15.7 Hz, H- $\beta$ ), 7.92 (1H, d, *J* = 15.7 Hz, H- $\alpha$ ), 7.39 (1H, d, *J* = 8.2 Hz, H-6), 6.33 (1H, dd, *J* = 8.2, 2.4 Hz, H-5), 6.32 (1H, d, *J* = 2.4 Hz, H-3), 5.99 (1H, s, H-3'), 5.03 (1H, t, *J* = 7.0 Hz, H-4''), 4.55 (2H, m, H-9''), 3.88 (3H, s, OCH<sub>3</sub>), 2.62 (1H, d, *J* = 2.7 Hz, H-1''a), 2.60 (1H, s, H-1''b), 2.54 (1H, m, H-2''), 2.05 (2H, t, *J* = 7.5 Hz, H-3''), 1.69 (3H, s, H-10''), 1.62 (3H, s, H-7''), 1.55 (3H, s, H-6''); <sup>13</sup>C-NMR (100 MHz, CD<sub>3</sub>OD)  $\delta$  : 195.6 (C=O), 167.4 (C-6'), 164.8 (C-4'), 163.2 (C-2'), 163.0 (C-4), 161.1 (C-2), 150.6 (C-8''), 140.6 (C- $\beta$ ), 132.6 (C-5''), 132.4 (C-6), 126.2 (C- $\alpha$ ), 125.8 (C-4''), 117.0 (C-1), 112.0 (C-9''), 109.7 (C-5'), 109.6 (C-5), 107.3 (C-1'), 104.4 (C-3), 92.3 (C-3'), 56.8 (OCH<sub>3</sub>), 48.8 (C-2''), 33.2 (C-3''), 28.9 (C-1''), 26.7 (C-7''), 19.8 (C-10''), 18.7 (C-6'').

#### Kuraridinol (9)

Amorphous orange powder; <sup>1</sup>H-NMR (400 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  : 14.84 (1H, s, OH-2'), 10.39 (1H, s, OH-4'), 10.18 (1H, s, OH-4), 9.93 (1H, s, OH-2), 7.94 (1H, d, *J* = 15.6 Hz, H- $\beta$ ), 7.85 (1H, d, *J* = 15.6 Hz, H- $\alpha$ ), 7.43 (1H, d, *J* = 8.6 Hz, H-6), 6.37 (1H, d, *J* = 2.4 Hz, H-3), 6.32 (1H, dd, *J* = 8.5, 2.4 Hz, H-5), 6.03 (1H, s, H-5'), 4.56 (1H, s, H-9''), 4.47 (1H, d, *J* = 2.2 Hz, H-9''), 3.83 (3H, s, OCH<sub>3</sub>), 2.55 (2H, m, H-1''), 2.35 (1H, m, H-2''), 1.64 (3H, s, H-10''), 1.35 (2H, m, H-3''), 1.19 (2H, m, H-4''), 1.02 (3H, s, H-6''), 1.01 (3H, s, H-7''); <sup>13</sup>C-NMR (100 MHz, DMSO-*d*<sub>6</sub>)  $\delta$  : 192.0 (C=O), 165.3 (C-4'), 162.6 (C-2'), 161.1 (C-4), 160.3 (C-6'), 159.0 (C-2), 148.0 (C-8''), 138.6 (C- $\beta$ ), 130.3 (C-6), 122.8 (C- $\alpha$ ), 113.8 (C-1), 110.9 (C-9''), 108.1 (C-5), 106.8 (C-3'), 104.5 (C-1'), 102.6 (C-3), 90.7 (C-5'), 68.7 (C-5''), 55.5 (OCH<sub>3</sub>), 46.4 (C-2''), 41.6 (C-4''), 29.5 (C-6''), 29.0 (C-7''), 27.1 (C-1''), 26.7 (C-3''), 17.9 (C-10'').

### Soya-cerebroside I (10)

Amorphous white powder; LR-FABMS :  $m/z$  759  $[M+2Na]^+$ , 736  $[M+Na]^+$ , 482 [long-chain base+glucose+Na] $^+$ ;  $^1H$ -NMR (400 MHz, pyridine- $d_5$ )  $\delta$  : 8.34 (1H, d,  $J$  = 8.7 Hz, NH), 5.98 (1H, dd,  $J$  = 15.4, 6.0 Hz, H-5), 5.90 (1H, dd,  $J$  = 15.8, 5.3 Hz, H-4), 5.48 (2H, t-like, H-8, 9), 4.90 (1H, d,  $J$  = 7.7 Hz, H-1"), 4.79 (1H, m, H-2), 4.75 (1H, t,  $J$  = 6.0 Hz, H-3), 4.69 (1H, dd,  $J$  = 10.5, 5.8 Hz, H-1b), 4.56 (1H, dd,  $J$  = 7.7, 3.6 Hz, H-2'), 4.50 (1H, dd,  $J$  = 11.7, 2.1 Hz, H-6"a), 4.34 (1H, dd,  $J$  = 11.7, 5.1 Hz, H-6"b), 4.22 (1H, dd,  $J$  = 10.4, 3.7 Hz, H-1a), 4.20 (2H, d,  $J$  = 9.1 Hz, H-3", 4"), 4.01 (1H, t,  $J$  = 8.1 Hz, H-2"), 3.89 (1H, m, H-5"), 2.13 (4H, m, H-6, 10), 1.99 (2H, m, H-7), 1.32 [brs,  $(CH_2)_n$ ], 1.24 [brs,  $(CH_2)_n$ ], 0.84 (6H, t-like,  $J$  = 6.5 Hz, H-18, 16');  $^{13}C$ -NMR (100 MHz, pyridine- $d_5$ )  $\delta$  : 175.6 (C-1'), 132.0 (C-5), 131.9 (C-4), 131.0 (C-9), 129.8 (C-8), 105.6 (C-1"), 78.5 (C-5"), 78.4 (C-3"), 75.1 (C-2"), 72.4 (C-2'), 72.2 (C-3), 71.5 (C-4"), 70.1 (C-1), 62.6 (C-6"), 54.5 (C-2), 35.6 (C-3'), 32.9 (C-7), 32.8-32.6 (C-6, 10), 32.0 (C-16, 14'), 29.5-29.9 (C-11-15, 4'-13'), 22.9 (C-17, 15'), 14.2 (C-18, 16').

### Methanolysis of compound 10

Compound **10** (10 mg) was refluxed with 0.9 N HCl in 82 % aqueous MeOH (3 mL) for 18 h. The resulting solution was extracted with *n*-hexane, and the combined organic phase was dried over  $Na_2SO_4$ . Evaporation of the hexane yielded a fatty acid methyl ester. The  $H_2O$  layer was neutralized with  $NH_4OH$  and extracted with ether. The ether layer was dried over  $Na_2SO_4$ , filtered, and then concentrated to yield a long-chain base. The *n*-hexane layer was removed and analyzed by GC. The retention times ( $t_R$ ) of the peaks were 24.958 min for fatty acid methyl ester. The fatty acid methyl ester was identified as 2-hydroxy hexadecanoic acid methyl ester.

### [(-)-Syringaresinol-4-O- $\beta$ -D-glucopyranoside] (11)

Amorphous powder;  $[\alpha]_D^{20}$  -2° (c 0.10, MeOH);  $^1H$ -NMR (400 MHz,  $CD_3OD$ )  $\delta$  : 6.70 (2H, s, H-2, 6), 6.64 (2H, s, H-2', 6'), 4.84 (1H, s, H-1"), 4.75 (1H, d,  $J$  = 3.3 Hz, H-7), 4.70 (1H, d,  $J$  = 3.8 Hz, H-7'), 4.27 (2H, dd,  $J$  = 15.2, 6.5 Hz, H-9'), 3.90 (2H, dd,  $J$  = 9.0, 2.5 Hz, H-9), 3.84 (6H, s,  $OCH_3 \times 2$ ), 3.83 (6H, s,  $OCH_3 \times 2$ ), 3.76 (1H, dd,  $J$  = 12.2, 2.3 Hz, H-6"a), 3.65 (1H, dd,  $J$  = 11.9, 5.1 Hz, H-6"b), 3.47 (1H, m, H-2"), 3.41 (1H, d,  $J$  = 2.4 Hz, H-4"), 3.39 (1H, d,  $J$  = 2.4 Hz, H-3"), 3.19 (1H, m, H-5"), 3.12 (2H, brs, H-8, 8');  $^{13}C$ -NMR (100 MHz,  $CD_3OD$ )  $\delta$  : 155.2 (C-3, 5), 150.1 (C-3', 5'), 140.3 (C-1), 137.0 (C-4'), 136.4 (C-4), 133.9 (C-1'), 106.1 (C-1"), 105.7 (C-2, 6), 105.3 (C-2', 6'), 88.4 (C-7'), 88.0 (C-7), 79.1 (C-5"), 78.6 (C-3"), 76.5 (C-2"), 73.7 (C-9), 73.6 (C-9'), 72.1 (C-4"), 63.4 (C-6"), 57.9 ( $OCH_3 \times 2$ ), 56.6 ( $OCH_3 \times 2$ ), 56.5 (C-8), 56.3 (C-8').

### Measurement of DPPH radical scavenging activity

The DPPH radical scavenging effect was evaluated as previous described by Blois (Blois, 1958) with minor modifications. A hundred sixty microliters ( $\mu L$ ) of MeOH solution of various sample concentrations was added to 40  $\mu L$  DPPH methanol solution ( $1.5 \times 10^{-4}$  M). After mixing gently and leaving for 30 min at room temperature, the optical density was measured at 520 nm using a microplate reader spectrophotometer VERSAmax (Molecular Devices, CA, USA). The antioxidant activity of each sample was expressed in terms of  $IC_{50}$  ( $\mu M$  required to inhibit DPPH radical formation by 50%) and calculated from the log-dose inhibition curve.

## RESULTS AND DISCUSSION

The EtOAc-soluble fraction of the MeOH extract of the stem bark of *A. julibrissin* was repeatedly chromatographed over Si gel, Sephadex LH-20, and RP-18 to yield compounds **1**~**11** (Fig. 1). Among them, compounds **3**~**9** and **11** were identified as luteolin (**3**) (Jung *et al.*, 2001; Watanabe, 1999), daidzein (**4**) (Agrawal and Bansal, 1989), sophoflavescenol (**5**) (Woo *et al.*, 1998), kurarionone (**6**), kurarinol (**7**), kuraridin (**8**), kuraridinol (**9**) (Ryu *et al.*, 1997; Ryu *et al.*, 1996; Kyogoku *et al.*, 1973), and (-)-syringaresinol-4-O- $\beta$ -D-glucopyranoside (**11**) (Kinjo *et al.*, 1991a; Higuchi *et al.*, 1992; Kinjo *et al.*, 1991b), respectively, by analysis of 1D and 2D NMR data including DEPT, COSY, HMQC, and HMBC techniques as well as by comparison with those of the literature values and/or by the direct comparison with the authentic samples. Compounds **3**~**9** are the first report from this plant.

Compound **1** was isolated as a yellow amorphous powder. The molecular formula of **1** was deduced as  $C_{16}H_{12}O_5$  based on the NMR and EIMS spectral data. Its UV spectrum exhibited characteristic absorbance bands of flavones at 237 nm and 337 nm. The presence of a hydroxyl group at C-7 was suggested from the bathochromic shift of band II with NaOAc (Mabry *et al.*, 1970). The EIMS spectrum of **1** showed a molecular ion peak at  $m/z$  284 and the *retro* Diels-Alder fragment ion peaks at  $m/z$  137  $[A_1+H]^+$  and  $m/z$  148  $[B_1]^+$  consistent with the presence of one hydroxyl group in ring-A, and both methoxy and hydroxyl groups in ring-B, respectively. The  $^1H$ -NMR spectrum of **1** showed signals due to a methoxy group at  $\delta$  3.89 (3H, s), H-3 at  $\delta$  6.83 (1H, s), and two aromatic ABX coupled systems at  $\delta$  7.86 (1H, d,  $J$  = 8.6 Hz), 6.90 (1H, dd,  $J$  = 8.7, 2.2 Hz), and 6.99 (1H, d,  $J$  = 2.2 Hz) assigned to H-5, -6, and -8, and  $\delta$  7.54 (1H, d,  $J$  = 2.2 Hz), 7.54 (1H, dd,  $J$  = 8.9, 2.2 Hz), and 6.93 (1H, d,  $J$  = 9.0 Hz) assigned to H-2', -6', and -5', confirming the presence of mono substitution in ring-A and disubstitution in ring-B. The methoxy group at  $\delta$  3.89 was found to be

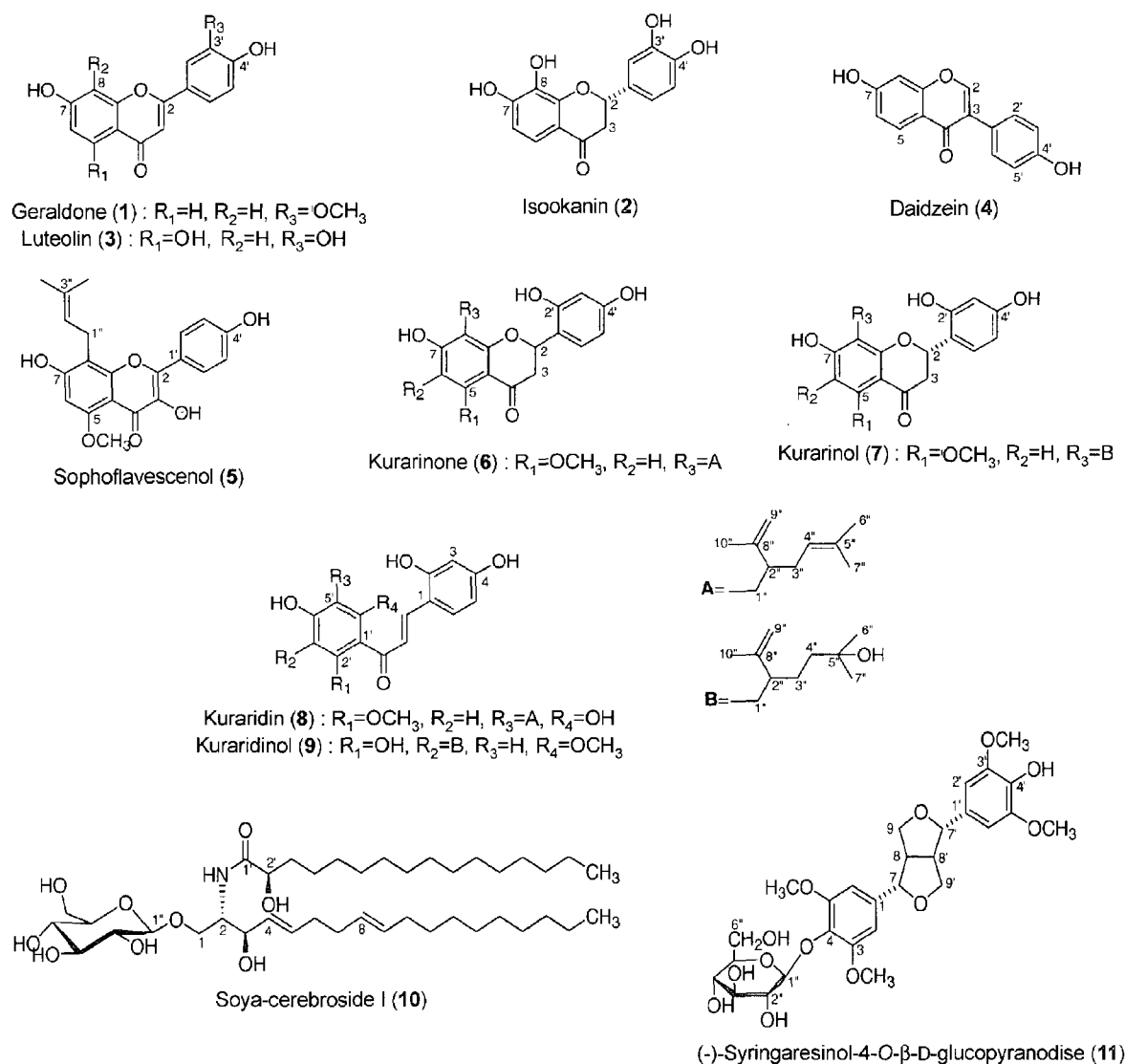


Fig. 1. Structures of compounds 1-11

attached to C-3' according to long-range C-H coupling between  $OCH_3$  and C-3' at  $\delta$  148.0 in the HMBC experiment. On the basis of the above evidences, compound 1 was determined as 3'-methoxy-7,4'-dihydroxyflavone (geraldone) and was further confirmed by the assignment of NMR data which was not previously reported, utilizing HMBC and HMQC experiments. Although geraldone has been previously isolated from *Trifolium subterraneum* L. (Wong and Francis, 1968), *Qualea parviflora*, *Q. grandiflora*, *Salvertia convallariodora*, *Vochysia tucanorum*, and *V. cinnamomea* (Lopes *et al.*, 1979), it is the first time to be isolated from *Albizzia* genus.

Compound 2 was obtained as an orange amorphous powder. The UV spectrum exhibited characteristic absorbance bands of flavanones at 233 (sh.) and 287 nm (Markham, 1982). Free hydroxyl groups at C-7 and 4' were suggested by the presence of shift of band II and I

with NaOAc and NaOMe, respectively (Mabry *et al.*, 1970). The  $^1H$ - and  $^{13}C$ -NMR spectral data also exhibited characteristic signals for the ABX system at  $\delta_H$  2.72 (dd,  $J = 16.9, 3.0$  Hz, H-3<sub>eq</sub>) and 3.06 (dd,  $J = 16.9, 12.4$  Hz, H-3<sub>ax</sub>) and  $\delta_H$  5.36 (dd,  $J = 12.4, 3.0$  Hz, H-2), along with an oxygen bearing methine at  $\delta_C$  82.4 (C-2), a carbonyl group at  $\delta_C$  194.8 (C-4) and a methylene at  $\delta_C$  45.9 (C-3), assigned to positions 2 and 3 on a flavanone (Marby *et al.*, 1970). The chemical shift value at  $\delta_C$  194.8, corresponding to a carbonyl resonance, indicated the absence of the hydroxyl group in position 5 (Ngadjui *et al.*, 2002). In the aromatic region of the  $^1H$ -NMR spectrum of 2, two aromatic protons at  $\delta$  7.29 and 6.51 (each 1H, d,  $J = 8.7$  Hz) were assigned to H-5 and -6 on the A-ring of flavanone skeleton, and one aromatic ABX spin coupled systems at  $\delta$  6.98 (1H, d,  $J = 1.7$  Hz), 6.85 (1H, dd,  $J = 8.2, 1.7$  Hz) and 6.78 (1H, d,  $J = 8.2$  Hz) revealed the presence of H-2',

-6', and -5', respectively. Chemical shifts and signal patterns in the NMR spectra indicated that the hydroxy groups were at C-7, -8, -3', and -4'. On the basis of the above evidences and the comparison of data with those of literature (Foo, 1987; Clark-Lewis and Porter, 1972), compound **2** was determined as (-)3',4',7,8-tetrahydroxyflavanone (isookanin). This is the first report of its occurrence in *Albizzia* genus.

Compound **10** was obtained as an amorphous powder. The molecular formula was deduced as  $C_{40}H_{75}NO_9$  based on a molecular ion at  $m/z$  736  $[M+Na]^+$  in the FAB-MS as well as the  $^{13}C$ -NMR and DEPT spectrum. The NMR data of **10** indicated the presence of  $\beta$ -D-glucose ( $\delta_H$  4.90, 1H, d,  $J = 7.7$  Hz, anomeric H;  $\delta_C$  105.6), an amide linkage ( $\delta_H$  8.34, 1H, d,  $J = 8.7$  Hz, N-H;  $\delta_C$  175.6) and two long chain aliphatic moieties which was essentially identical to those of cerebrosides from *Arisaema amurense* (Jung *et al.*, 1996), suggesting a sphingosine-type cerebroside nature (Jung *et al.*, 1996; Inagaki *et al.*, 1998). The positive FAB-MS spectrum of **10** showed an ion [long-chain base+glucose+Na] $^+$  peak at  $m/z$  482 typical for amide bond cleavage in cerebrosides (Kang *et al.*, 2001; Inagaki *et al.*, 1998). Therefore, **10** was expected to be a sphingosine-type cerebroside having 2-hydroxypalmitic acid  $\beta$ -D-glucopyranose residue. The amide signal at  $\delta$  8.34 gave a cross peak with the H-2 multiplet signal at  $\delta$  4.79 in the  $^1H$ - $^1H$  COSY spectrum of **10**, which in turn showed cross peaks with methylene protons (H-1) at  $\delta$  4.22, 4.69, and  $\delta$  4.75 (H-3). The latter correlated with two olefinic proton signals at  $\delta$  5.98 (H-5) and 5.90 (H-4). The double bond at C-4 (5) was found to be *trans* (*E*), as evidenced by the large coupling constant ( $J = 15.4$  Hz). These results were in good agreement with those of known (2*S*,3*R*,4*E*)-sphingosine-type cerebrosides (Jung *et al.*, 1996; Inagaki *et al.*, 1998), which were further supported by the  $^{13}C$ -NMR data. The chemical shift of three methylene carbons (C-6, 7 and 10) adjacent to the olefinic carbons were observed at  $\delta$  32.0-33.0, supporting the *trans* (*E*) double bond at C-8 and 9 (Kang *et al.*, 2001; Inagaki *et al.*, 1998). The relative configurations of C-2, 3 and C-2' of **10** were established on the basis of  $^{13}C$ -NMR data [ $\delta$  54.5 (C-2), 72.2 (C-3) and  $\delta$  72.4 (C-2')], which were in good agreement with those published for 2*S*,3*R*,2'*R* configuration (Jung *et al.*, 1996; Inagaki *et al.*, 1998). The methanolysis with HCl in MeOH of **10** yielded 2-hydroxy-hexadecanoic acid methyl ester, which was identified by the GC-MS analysis. In light of the above evidences, the structure of **10** was deduced to be 1-O- $\beta$ -D-glucopyranosyl-(2*S*,3*R*,4*E*,8*E*)-2-[(2*R*)-2-hydroxyhexadecanoylamino]-4,8-octadecadiene-1,3-diol. This compound was found to be identical with the known soya-cerebroside I, which has been previously isolated from *Phaseolus angularis* (Ohnishi and Fujino, 1981), soybean (Shibuya *et al.*, 1990), *Tetragonia tetragonoides* (Okuyama and Yamazaki, 1983),

*Pisum sativum* (Ito *et al.*, 1985), *Acer negundo* (Inoue *et al.*, 1992), *Prunus jamasakura* (Yoshioka *et al.*, 1990), *Allium sativum* (Inagaki *et al.*, 1998), *Dimocarpus fumatus* (Voutquenne *et al.*, 1999), *Momordica charantia* (Xiao *et al.*, 2000), and *Trichosanthes kirilowii* (Kim *et al.*, 2001). This seems to be the first instance of the isolation of soya-cerebroside I from *Albizzia* genus.

The compounds **2** and **3** exhibited strong antioxidative activity on the DPPH radical with  $IC_{50}$  values of 3.89 and 1.70  $\mu$ M, respectively. Their  $IC_{50}$  values were two times and four times lower than the  $IC_{50}$  value of 8.46  $\mu$ M for L-ascorbic acid, respectively. Also compound **11** showed scavenging activity on the DPPH radical with  $IC_{50}$  value of 10.46  $\mu$ M, while other compounds did not show scavenging activity on the DPPH radical.

## ACKNOWLEDGEMENTS

The high resolution positive ion FAB-MS spectra were provided by the Korea Basic Science institute. This study was supported by a grant from the Ministry of Health & Welfare, Republic of Korea (01-PJ2-PG6-01NA01-0002).

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