An 80% aqueous acetone extract of *Cassia auriculata* leaves was found to show a protective effect on d-galactosamine-induced cytotoxicity in primary cultured mouse hepatocytes. From the 80% aqueous acetone extract, we isolated a new benzocoumarin glycoside, avaraoside I (1), and a new flavanol dimer, avaraol I (2), together with 29 known constituents. The structures of the new compounds were elucidated on the basis of chemical and physicochemical evidence. In addition, three isolated compounds, pseudosemiglabrin (15, 0.0011%), (2S)-7,4′-dihydroxyflavan(4β→8)-catechin (22, 0.00075%), and (2S)-7,4′-dihydroxyflavan(4β→8)-gallocatechin (23, 0.092%), displayed hepatoprotective effects equivalent to that of the hepatoprotective agent, silybin.

**Key words** *Cassia auriculata*; avaraoside I; avaraol I; Ayurvedic traditional medicine; hepatoprotective effect.
October 2014 1027

spectrum (HR-MS) and $^{13}$C-NMR data. Acid hydrolysis of I liberated d-glucose and l-rhamnose, which were identified by HPLC analysis using an optical rotation detector. The $^1$H- (acetone-$d_6$) and $^{13}$C-NMR (Table 1) spectra of I, which were assigned by various NMR experiments, showed signals ascribable to a methyl [δ 2.79 (3H, s, CH$_3$-5)], an olefinic proton [δ 6.03 (1H, s, H-3)], three aromatic protons [δ 6.64, 6.75 (1H each, both d, J=2.0 Hz, H-7, 9), 7.30 (1H, s, H-6)], an α-L-rhamnopyranosyl moiety [δ 4.79 (1H, br s, H-1)], and a β-D-glucopyranosyl moiety [δ 5.38 (1H, d, J=7.3 Hz, H-1’)]. The proton and carbon signals of I in the $^1$H- and $^{13}$C-NMR spectra resembled those of pannorin, a naphthopyrone, except for the signals due to the glycosyl moiety, which were similar to those of rutin (12). In the heteronuclear multiple bond connectivity (HMBC) experiment, long-range correlations were observed between the following protons and carbons: H-3 and C-2, 4, 4a; H-6 and C-4a, 6a, 7, 10a; H-7 and C-6, 8, 9, 10a; H-9 and C-7, 8, 10, 10a; CH$_3$-5 and C-4a, 5, 6; H-1’ and C-6’ (Fig. 2). Furthermore, in the nuclear Overhauser effect spectroscopy (NOESY) experiment, NOE correlations were observed between the following proton pairs: H-6 and H-7; C$_3$H-5 and H-6; and H-1’ and H-3 (Fig. 2). On the basis of all these pieces of evidence, the chemical structure of avaraoside I (I) was determined to be pannorin 4-O-α-L-rhamnopyranosyl(1→6)-β-D-glucopyranoside.

Avaraol I (2), obtained as a yellow amorphous powder with a positive optical rotation ([α]$^D$+146.6 in MeOH), showed absorption bands ascribable to hydroxy and aromatic ring

### Table 1. $^{13}$C-NMR Spectroscopic Data for Compounds 1 and 2 in Acetone-$d_6$

<table>
<thead>
<tr>
<th>Position</th>
<th>1-Aglycon</th>
<th>1-$β$-$D$-Glucopyranosyl</th>
<th>Position</th>
<th>2-Aglycon</th>
<th>2-$β$-$D$-Glucopyranosyl</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Aglycon</td>
<td>β-$D$-Glucopyranosyl</td>
<td></td>
<td>Upper unit</td>
<td>Lower unit</td>
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<tr>
<td>2</td>
<td>163.0</td>
<td>1’</td>
<td>2</td>
<td>76.1</td>
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<td>3</td>
<td>91.2</td>
<td>2’</td>
<td>3</td>
<td>35.5</td>
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<tr>
<td>4a</td>
<td>108.5</td>
<td>4’</td>
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<td>5</td>
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<td>6</td>
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<td>6</td>
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<td>7</td>
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<td>7’</td>
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<td>6a</td>
<td>139.2</td>
<td>α-L-Rhamnopyranosyl</td>
<td>8</td>
<td>104.1</td>
<td>8’</td>
</tr>
<tr>
<td>7</td>
<td>102.6</td>
<td>1’</td>
<td>9</td>
<td>156.7</td>
<td>9’</td>
</tr>
<tr>
<td>8</td>
<td>160.3</td>
<td>2’</td>
<td>10</td>
<td>115.9</td>
<td>10’</td>
</tr>
<tr>
<td>9</td>
<td>104.1</td>
<td>3’</td>
<td>11</td>
<td>133.9</td>
<td>1’</td>
</tr>
<tr>
<td>10</td>
<td>156.7</td>
<td>4’</td>
<td>12</td>
<td>127.9</td>
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<tr>
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<td>5’</td>
<td>13</td>
<td>115.9</td>
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<tr>
<td>10b</td>
<td>154.8</td>
<td>6’</td>
<td></td>
<td>158.0</td>
<td>4’</td>
</tr>
</tbody>
</table>

Fig. 1. Structures of Constituents Isolated from the Leaves of C. auriculata

![avaraoide I (1)]

![varaol I (2)]

![20: R = H](21: R = Me)

![22: R = H](23: R = OH)

![26: R = OH](27: R = OH)

![28: R = OMe](29)

![30](31)

Glc: β-D-glucopyranosyl Rut: 6-O-(α-L-rhamnopyranosyl)-β-D-glucopyranosyl Api: β-D-apiofuranosyl
The proton and carbon signals of $^{10}$acetone-flavanol dimers such as (2) resembled those of functionalities in the IR spectrum, respectively. FAB-MS in Table 2. Effects of Constituents on n-GalN-Induced Cytotoxicity in Primary Cultured Mouse Hepatocytes$^{39}$

<table>
<thead>
<tr>
<th>Treatment conc. (µM)</th>
<th>Inhibition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>11</td>
<td>-2.1±1.2</td>
</tr>
<tr>
<td>13</td>
<td>-2.2±1.2</td>
</tr>
<tr>
<td>14</td>
<td>2.4±1.4</td>
</tr>
<tr>
<td>15</td>
<td>4.6±1.9</td>
</tr>
<tr>
<td>16</td>
<td>3.1±2.4</td>
</tr>
<tr>
<td>17</td>
<td>0.6±3.6</td>
</tr>
<tr>
<td>18</td>
<td>-2.4±3.2</td>
</tr>
<tr>
<td>19</td>
<td>16.0±5.3*</td>
</tr>
<tr>
<td>20</td>
<td>5.2±2.5</td>
</tr>
<tr>
<td>21</td>
<td>16.0±4.0</td>
</tr>
<tr>
<td>22</td>
<td>-3.2±3.3</td>
</tr>
<tr>
<td>23</td>
<td>1.5±0.8</td>
</tr>
<tr>
<td>24</td>
<td>2.0±4.7</td>
</tr>
<tr>
<td>25</td>
<td>0.0±0.3</td>
</tr>
<tr>
<td>26</td>
<td>4.0±3.6</td>
</tr>
</tbody>
</table>

Silybin$^{36,37}$

- Each value represents the mean±S.E.M. (N=4). Significantly different from control, *p<0.05, **p<0.01. b) Reference compound.$^{39}$ Compounds 12, 26, and 27 did not show any effect at 100.µM. IC_{50} values (µM) of compounds 15, 22, 23, and silybin$^{36}$ were 45.2, 44.6, 50.6, and 38.8, respectively.

Table 2. Effects of Constituents on n-GalN-Induced Cytotoxicity in Primary Cultured Mouse Hepatocytes

The proton and carbon signals of $^{10}$acetone-flavanol dimers such as (2) showed signals assignable to two methines with an oxygen function [δ 4.75 (1H, dd, J=2.2, 10.1Hz, H-2’), 5.38 (1H, dd, J=3.4, 6.4Hz, H-2)], and 10 aromatic protons [δ 6.01 (1H, s, H-6’), 6.33 (1H, dd, J=2.5, 8.6Hz, H-6), 6.43 (1H, d, J=2.5Hz, H-8), 6.49 (2H, s, H-2”‘, 6”‘), 6.76 (1H, d, J=8.6Hz, H-5), 6.81 (2H, d, J=8.6Hz, H-3‘, 5’), 7.22 (2H, d, J=8.6Hz, H-2‘, 6’)]. The structure of 2 was characterized by means of double quantum filter correlation spectroscopy (DQF COSY) and HMBC experiments (Fig. 1). The DQF COSY data of 2 indicated the presence of the partial structures (bold lines), and long-range correlations in the HMBC experiment were observed between the following protons and carbons: H-2 and C-1’, 2’, 6’; H-3 and C-10, 8’; H-4 and C-2, 5, 8’; H-5 and C-7, 9; H-6 and C-8; H-8 and C-6, 7, 9; H-2’; 6’ and C-4’; H-3’, 5’ and C-1’, 4’; H-2”‘ and C-1”‘, 2”‘, 6”‘; H-3”‘ and C-10”; H-4”‘ and C-2”, 5”, 9”, 10”; H-6”‘ and C-5”, 7’, 8’; H-2”‘, 6”‘ and C-1”, 3”, 4”. The proton and carbon signals of 2 in the $^1$H- and $^{13}$C-NMR spectra resembled those of 23 and 25, except for the signals around the 3’-position. On the basis of the above results and the comparison of the NMR data for 2 with those of known flavanol dimers such as (2S)-3’,4’,7-trihydroxyflavan(4β→8)catechin,$^{55}$ the planar structure of 2 was determined. The relative stereostructure between 2- and 4-positions in 2 was characterized by NOESY experiment, which showed NOE correlations between the following proton pairs: H-2 and H-3β, H-3α and H-4. The configuration at the 4-position in 2 was determined by circular dichroism (CD) measurement. It was reported that the configuration at the 4-position of the flavanol dimer, in which a linkage is formed between the 4-position of upper flavanol and the 8-position of lower flavanol, was deduced from the Cotton effect around 240nm in the CD spectrum.$^{36,37}$ The CD spectrum of 2 showed a positive Cotton effect at 239nm ($\Delta e$+17.07), similar to that of a known flavanol dimer with an R-configuration at the 4-position, (−)-epiafzelechin-(4β→8)-4β-carboxymethyl-(−)-epicatechin methyl ester [234nm ($\Delta e$+17.19)].$^{36,37}$ So that the 4-position of 2 was found to possess an R-configuration. On the basis of all these pieces of evidence, the chemical structure of avaranol I (2) was determined to be (2S)-7,4’-dihydroxyflavan(4β→8)-(2S)-5,3’,4’,5’-pentahydroxyflavan.

Recently, we have reported the isolation of several constituents with hepatoprotective effects from medicinal plants, including Salacia chinensis,$^{38}$ Cistanche tubulosa,$^{39}$ Hedychium coronarium,$^{40}$ Sinocrassula indica,$^{41}$ Piper chaba,$^{42}$ Camellia sinensis,$^{43}$ Sedum sarmentosum,$^{44,45}$ and Rhodiola sachalinensis.$^{46}$ In addition, we have reported that flavonoids and their glucosides, 3, 4, 5, 8, and 9, showed hepatoprotective...
effects.41) As a continuing exploratory study of the hepato-
protective constituents from natural products, the protective
effects of the principal constituents, 11–19, 22–28, on
n-GalN-induced cytotoxicity in primary cultured mouse hepatocytes
were examined. As shown in Table 2, compounds 15, 19, 22,
and 23 exhibited significant protective effects [inhibition (%) 15:
37.0±3.7 (p<0.01), 19: 24.4±3.1 (p<0.01), 22: 33.5±2.9
(p<0.01), and 23: 28.2±4.7 (p<0.01) at 30 µM, respectively].
The effects were equivalent to that of the reference compound,
silybin [45±2.8 (p<0.01) at 30 µM].41) On the other hand,
compounds 11–13 showed weak or no effects. We have re-
ported that the effects of 3-O-mono-glycosides 8 and 9 were
stronger than those of corresponding aglycones 4 and 5.41) In
the present study, the effects of 8 and 9 were also found to be
stronger than those of corresponding 3-0-rutinosides 11 and 12.
Furthermore, among the catechin dimers, 22–25, the hepato-
protective effects of 22 and 23 having the S-configuration at
3β-position were stronger than those of 24 and 25 having the
R-configuration at 3α-position.

Experimental
General Experimental Procedures
The following instruments were used to obtain physical data: specific rotations, a Horiba SEPA-300 digital polarimeter (l=5 cm); IR spectra, a Shimadzu FTIR-8100 spectrophotometer; CD spectra, a JASCO J-810 spectrometer; 1H-NMR spectra, JEOL EX-270 (270 MHz), FAB-MS and HR-FAB-MS, a JEOL JMS-SX 102 A mass spectrometer; electron ionization-mass spectra (EI-MS), Shimadzu FTIR-8100 spectrometer; CD spectra, a JASCO J-
18 tungsten halogen lamp. A voucher of the plant is on file in our laboratory.

Extraction and Isolation
The dried leaves of C. auriculata (1.5 kg), which were cultivated in India, were purchased from N.T.H. Co., Ltd. A voucher of the plant is on file in our laboratory.

The dried leaves of C. auriculata (1.5 kg) were finely cut and extracted three times with 80% aqueous acetone under room temperature for 12 h. Evap-
oration of the solvent under reduced pressure provided the 80% aqueous acetone extract (407.7 g, 27.2%). A part of the extract (377.7 g) was partitioned into an EtOAc–H₂O (1:1, v/v) mixture to furnish an EtOAc-soluble fraction (164.1 g, 11.8%) and aqueous layer. The aqueous layer was extracted with n-BuOH to give n-BuOH- (63.7 g, 4.6%) and H₂O- (149.9 g, 10.8%) soluble fractions.

A part of the EtOAc-soluble fraction (144.1 g) was subjected to normal-phase silica gel column chromatography [2.5 kg, n-hexane–EtOAc (10:1+5:1+2:1+1:1+1:2, v/v)→CHCl₃–MeOH–H₂O (10:3:1, lower layer→7:3:1, lower layer→6:4:1, v/v)→MeOH] to give 8 fractions [Fr. 1 (1.92 g), Fr. 2 (10.19 g), Fr. 3 (2.09 g), Fr. 4 (2.66 g), Fr. 5 (9.27 g), Fr. 6 (65.07 g), Fr. 7 (14.54 g), Fr. 8 (35.70 g)]. Fraction 1 (1.92 g) was separated by reversed-phase silica gel column chromatography [60 g, MeOH–H₂O (40:60→60:40→75:25, v/v)→MeOH] to give 7 fractions [Fr. 1–1 (18 mg), Fr. 1–2, Fr. 1–3, Fr. 1–4, Fr. 1–5, Fr. 1–6, Fr. 1–7]. Fraction 1–1 (18 mg) was purified by HPLC [COSMOSIL-5C₁₈-PAQ, MeOH–H₂O (80:20, v/v)] to give chrysophanol (26, 5.0 mg). A part of fraction 2 (4.45 g) was separated by reversed-phase silica gel column chromatography [60 g, MeOH–H₂O (40:60→60:40→75:25→90:10, v/v)→MeOH] to give 4 fractions [Fr. 2–1, Fr. 2–2 (43 mg), Fr. 2–3 (799 mg), Fr. 2–4]. Fraction 2–2 (43 mg) was purified by HPLC [COSMOSIL-5C₁₈-PAQ, MeOH–H₂O (85:15, v/v)] to give physcion (28, 19 mg). Fraction 3 (2.09 g) was separated by reversed-phase silica gel column chromatography [60 g, MeOH–H₂O (30:70→50:50→70:30→90:10, v/v)→MeOH] to give 9 fractions [Fr. 3–1, Fr. 3–2, Fr. 3–3, Fr. 3–4 (61 mg), Fr. 3–5 (59 mg), Fr. 3–6, Fr. 3–7, Fr. 3–8, Fr. 3–9]. Fraction 3–4 (61 mg) was purified by HPLC [COSMOSIL-5C₁₈-PAQ, MeOH–H₂O (65:35, v/v)] to give pseudosemiglabrin (15, 13 mg) and 21 (16 mg). Fraction 3–5 (59 mg) was purified by HPLC [COSMOSIL-5C₁₈-PAQ, MeOH–H₂O (65:35, v/v)] to give lancelotin B (14, 18 mg). Fraction 4 (2.66 g) was separated by reversed-phase silica gel column chromatography [80 g, MeOH–H₂O (15:85→30:70→45:55→60:40→75:25, v/v)→MeOH] to give 12 fractions [Fr. 4–1, Fr. 4–2, Fr. 4–3, Fr. 4–4 (114 mg), Fr. 4–5 (309 mg), Fr. 4–6 (152 mg), Fr. 4–7, Fr. 4–8, Fr. 4–9, Fr. 4–10, Fr. 4–11, Fr. 4–12]. Fraction 4–4 (114 mg) was purified by HPLC [COSMOSIL-5C₁₈-PAQ, MeOH–H₂O (40:60, v/v)] to give myricetin (6, 8.5 mg) and isorcorcin (9, 12 mg). Fraction 4–5 (309 mg) was purified by HPLC [COSMOSIL-5C₁₈-PAQ, 1] MeOH–H₂O (55:45, v/v), [2] CH₃CN–H₂O (30:70, v/v) to give luteolin (3, 122 mg), quercetin (5, 15 mg), 3-methoxyxutelin (7, 22 mg), and 6-demethylxipalicarpin (20, 13 mg). Fraction 4–6 (152 mg) was purified by HPLC [COSMOSIL-5C₁₈-PAQ, MeOH–H₂O (50:50, v/v)] to give kaempferol (4, 32 mg). Fraction 5 (9.27 g) was separated by reversed-phase silica gel column chromatography [280 g, MeOH–H₂O (15:85→30:70→45:55→60:40→75:25→90:10, v/v)→MeOH] to give 14 fractions [Fr. 5–1, Fr. 5–2 (260 mg), Fr. 5–3 (316 mg), Fr. 5–4, Fr. 5–5, Fr. 5–6, Fr. 5–7, Fr. 5–8, Fr. 5–9 (323 mg), Fr. 5–10, Fr. 5–11, Fr. 5–12, Fr. 5–13, Fr. 5–14]. Fraction 5–2 (260 mg) was purified by HPLC [COSMOSIL-5C₁₈-PAQ, MeOH–H₂O (20:80, v/v)] to give (+)-catechin (16, 46 mg). Fraction 5–3 (316 mg) was purified by HPLC [COSMOSIL-5C₁₈-PAQ, MeOH–H₂O (25:75, v/v)] to give (−)-epicatechin (18, 73 mg). Fraction 5–9 (323 mg) was purified by HPLC [COSMOSIL-5C₁₈-PAQ, MeOH–H₂O (50:50, v/v)] to give avaranol I (2, 8.7 mg), 22 (9.2 mg), and 24 (8.6 mg). A part of fraction 6 (50.0 g) was separated by reversed-phase silica gel column chromatography [1.5 kg, MeOH–H₂O (15:85→30:70→50:50→70:30, v/v)→MeOH] to give 14 fractions [Fr. 6–1, Fr. 6–2, Fr. 6–3 (1.23 g), Fr. 6–4, Fr. 6–5, Fr. 6–6, Fr. 6–7, Fr. 6–8, Fr. 6–9, Fr. 6–10, Fr. 6–11, Fr. 6–12].
Fraction 6-3 (1.23 g) was purified by HPLC [COSMOSIL-5C\(\alpha\)-PAQ, MeOH–H\(_2\)O (15:85, v/v)] to give (+)-gallocatechin (17, 81 mg). Fraction 6-5 (768 mg) was purified by HPLC [COSMOSIL-5C\(\alpha\)-PAQ, MeOH–H\(_2\)O (20:80, v/v)] to give (−)-epigallocatechin (19, 26 mg). A part of Fr. 6-7 (500 mg) was purified by HPLC [COSMOSIL-5C\(\alpha\)-PAQ, MeOH–H\(_2\)O (35:65, v/v)] to give 23 (65 mg). A part of Fr. 6-9 (630 mg) was purified by HPLC [COSMOSIL-5C\(\alpha\)-PAQ, MeOH–H\(_2\)O (40:60, v/v)] to give 25 (15 mg). A part of fraction 6-12 (580 mg) was purified by HPLC [COSMOSIL-5C\(\alpha\)-PAQ, MeOH–H\(_2\)O (50:50, v/v)] to give 8 (13 mg). A part of fraction 6-13 (800 mg) was purified by HPLC [COSMOSIL-5C\(\alpha\)-PAQ, MeOH–H\(_2\)O (40:60, v/v)] to give rutin (12, 129 mg). Fraction 7 (14.54 g) was separated by reversed-phase silica gel column chromatography [420 g, MeOH–H\(_2\)O (30:70→45:55→60:40→75:25, v/v)] to give 12 fractions [Fr. 7-1, Fr. 7-2 (846 mg), Fr. 7-3 (856 mg), Fr. 7-4, Fr. 7-5, Fr. 7-6, Fr. 7-7, Fr. 7-8, Fr. 7-9, Fr. 7-10, Fr. 7-11, Fr. 7-12]. Fraction 7-2 (846 mg) was purified by HPLC [COSMOSIL-5C\(\alpha\)-PAQ, MeOH–H\(_2\)O (40:60, v/v)] to give 10 (20 mg, 0.0016%) and rutin (12, 55 mg). A part of Fr. 7-3 (120 mg) was purified by HPLC [COSMOSIL-5C\(\alpha\)-PAQ, MeOH–H\(_2\)O (45:55, v/v)] to give rutin (12, 64 mg). A part of fraction 8 (30.0 g) was separated by reversed-phase silica gel column chromatography [600 g, MeOH–H\(_2\)O (30:70→45:55→60:40→75:25, v/v)] to give 11 fractions [Fr. 8-1, Fr. 8-2, Fr. 8-3, Fr. 8-4, Fr. 8-5, Fr. 8-6 (708 mg), Fr. 8-7 (51.6 mg), Fr. 8-8, Fr. 8-9, Fr. 8-10, Fr. 8-11]. A part of Fr. 8-6 (100 mg) was purified by HPLC [COSMOSIL-5C\(\alpha\)-PAQ, MeOH–H\(_2\)O (40:60, v/v)] to give rutin (12, 64 mg). A part of Fr. 8-7 (100 mg) was purified by HPLC [COSMOSIL-5C\(\alpha\)-PAQ, MeOH–H\(_2\)O (40:60, v/v)] to give rutin (12, 49 mg). A part of the n-BuOH-soluble fraction (53.7 g) was subjected to reversed-phase silica gel column chromatography [1.2 kg, MeOH–H\(_2\)O (15:85→30:70→45:55→60:40→75:25, v/v)] to give 10 fractions [Fr. 1, Fr. 2, Fr. 3 (3.09 g), Fr. 4, Fr. 5 (3.76 g), Fr. 6, Fr. 7, Fr. 8 (4.72 g), Fr. 9, Fr. 10]. A part of fraction 3 (800 mg) was purified by HPLC [YMC-Pack ODS-A, MeOH–H\(_2\)O (25:75, v/v)] to give roseosea (29, 4.2 mg), (30, 14 mg), and (31, 4.4 mg). A part of fraction 5 (800 mg) was purified by HPLC [COSMOSIL-5C\(\alpha\)-PAQ, MeCN–H\(_2\)O (20:80, v/v)]. 2 MeOH–H\(_2\)O (35:65, v/v)] to give avarasiode I (1, 13 mg) and I2 (13 mg). A part of fraction 8 (200 mg) was purified by HPLC [COSMOSIL-5C\(\alpha\)-PAQ, MeCN–H\(_2\)O (20:80, v/v)] to give 11 (18 mg) and rutin (12, 45 mg).

Avarasiode I (1) a yellow powder; \([\alpha]_{D}^{25} = -88.2^\circ \) (c = 0.6, MeOH); UV (MeOH) \(\lambda_{max}\) (log \(\varepsilon\)) 327 (3.76), 292 (4.02), 235 (4.24) nm; IR (KBr) \(\nu_{max}\) 3423, 1717, 1619, 1509, 1069 cm\(^{-1}\); \(^{1}H\)-NMR (acetone-\(d_{6}\), 600 MHz) \(\delta\) 2.79 (3H, s, \(CH_{3}\)-5), 4.79 (1H, br s, H-1\(^{\uparrow}\)), 5.38 (1H, d, \(J = 7.3\) Hz, H-1\(^{\downarrow}\)), 6.03 (1H, s, H-3\(^{\uparrow}\)), 6.64 (1H, d, \(J = 2.0\) Hz, H-9), 6.75 (1H, d, \(J = 2.0\) Hz, H-7), 7.30 (1H, s, H-6); \(^{13}C\)-NMR data see Table 1; positive-ion FAB-MS \(m/z\) 567 [M+H\(^{+}\)]; HR-FAB-MS: \(m/z\) 567.1706 (Caled for \(C_{39}H_{30}O_{11}[M+H\(^{+}\)]^+, 567.1713)).

Avarasil (2) a yellow powder; \([\alpha]_{D}^{25} = +146.6^\circ \) (c = 0.7, MeOH); UV (MeOH) \(\lambda_{max}\) (log \(\varepsilon\)) 281 (3.90), 230 (4.67) nm; CD (MeOH) \(\lambda_{max}\) (Ae) 274 (-3.03), 239 (+17.07) nm; IR (KBr) \(\nu_{max}\) 3430, 1509 cm\(^{-1}\); \(^{1}H\)-NMR (acetone-\(d_{6}\), 500 MHz) \(\delta\) 1.89, 2.10 (1H each, both m, H-2\(^{\pm}\)), 2.28 (1H, m, H-3\(\alpha\)), 2.55 (1H, m, H-3\(\beta\)), 2.61 (2H, m, H-4\(^{-}\)), 4.51 (1H, dd like H-4\(\alpha\)), 4.75 (1H, dd, \(J = 2.2, 10.1\), H-2\(^{-}\)), 5.38 (1H, dd, \(J = 3.4, 6.4\), H-2\(^{+}\)), 6.01 (1H, s, H-6\(^{\downarrow}\)), 6.33 (1H, dd, \(J = 2.5, 8.6\) Hz, H-6\(^{\downarrow}\)), 6.43 (1H, d, \(J = 2.5\) Hz, H-8), 6.49 (2H, s, H-2\(^{\alpha,\beta}\)), 6.76 (1H, d, \(J = 8.6\) Hz, H-5), 6.81 (2H, d, \(J = 8.6\) Hz, H-3\(^{\prime}\)), 7.22 (2H, d, \(J = 8.6\) Hz, H-2\(^{\prime}\)), \(^{1}C\)-NMR data see Table 1; positive-ion FAB-MS \(m/z\) 553 [M+Na\(^{+}\)]; HR-FAB-MS: \(m/z\) 553.1472 (Caled for \(C_{39}H_{30}O_{11}Na^{+}[M+Na\(^{+}\)]^+, 553.1475).
34) The 1H- and 13C-NMR spectra of 1 and 2 were assigned with the aid of distortionless enhancement by polarization transfer (DEPT), DQF COSY, heteronuclear multiple quantum coherence spectroscopy (HMQC), and HMBC experiments.