SIALIDASE INHIBITORY ACTIVITY OF SYNTHESIZED BIFLAVONOID GLYCOCONJUGATES

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Abstract – Ginkgetin (1) and sciadopitysin (2) have been shown to exhibit influenza virus sialidase inhibitory activity. We report the synthesis and sialidase inhibitory activity of glycoconjugates consisting of biflavonoids (1, 2) and sugars: 2-keto-3-deoxy-D-glycero-D-galactonononic acid (KDN, 3), N-acetyl-D-glucosamine (GlcNAc, 4), and N-acetyl-D-lactosamine (LacNAc, 5). The glycoconjugates (18R, 18S, 21R, 21S) of biflavonoids (1, 2) and GlcNAc (4) showed selective inhibitory activity against sialidase of influenza A virus H1N1 subtype. In particular, the inhibitory activity of 18S was similar to or higher than that of 5,7,4′-trihydroxy-8-methoxyflavone (F36) as a positive control. The glycoconjugate 18S showed the most potent inhibitory activity against sialidase of influenza A virus H1N1 subtype, with an IC50 of 48.5 µg/mL.

A flavonoid, 5,7,4′-trihydroxy-8-methoxyflavone (F36) isolated from Scutellaria baicalensis Georgi, and two biflavonoids, ginkgetin (1) isolated Cephalotaxus harringtonii (Knight ex J.Forbes) K. Koch and sciadopitysin (2) isolated from Sciadopitys verticillata (Thunb.) old & Zucc., display influenza virus
sialidase inhibitory activity among natural compounds (Figure 1).\textsuperscript{1,2} The glycoconjugates consisting of biflavonoids (1, 2) linked to \textit{N}-acetylneuraminic acid (Neu5Ac, 6) have been synthesized and display strong anti-influenza virus activity by inhibition of influenza virus sialidase, also known as neuraminidase (NA), the enzyme involved in release of progeny virus from host cells (Figure 2).\textsuperscript{2,3}

Neu5Ac (6) is a typical sialic acid, an acidic monosaccharide consisting of nine carbon atoms, that is found in various animal tissues. 2-Keto-3-deoxy-\textit{d}-glycero-\textit{d}-galactonononic acid (KDN, 3) is a sialic acid in which the \textit{N}-acetyl group of 6 is replaced by a hydroxy group. \textit{N}-Acetyl-\textit{d}-glucosamine (GlcNAc, 4) and \textit{N}-acetyl-\textit{d}-lactosamine (LacNAc, 5), which is a linked galactose and 4, are sugars containing the \textit{N}-acetyl group. In addition, the binding of influenza virus to erythrocytes is mediated by the interaction of the influenza virus hemagglutinin (HA) with cell surface receptors, containing sialyl oligosaccharides consisting of sugars, such as 5 and 6.\textsuperscript{4} Since the glycoconjugates containing 6 have sialidase inhibitory activity, we synthesized glycoconjugates consisting of the biflavonoids (1, 2) linked to sugars (3-5) and evaluated their biological activity.

\textbf{Figure 1.} Structures of F36 and biflavonoids (1, 2)

\textbf{Figure 2.} Structures of sugar moieties in glycoconjugates
Sugar donors (8, 9) were used as chlorides of sugar with hydroxy groups by way of acetyl groups. The KDN-Ac donor 8 was prepared from KDN-Ac 7 by acetyl chloride (AcCl) and HCl gas (Scheme 1). The GlcNAc-Ac donor 9 was used as a commercial reagent. To a solution of biflavonoids (1, 2) in dry DMF were added sodium hydride and protected sugar donors (8, 9) under Ar gas at room temperature (Scheme 2). When the sugar was combined with the C-7" position of 1 and 2, it caused a stereochemical obstruction to yield atropic isomers (R and S formation). Synthesized and separated compounds of absolute stereochemistry were determined by empirical interpretation of ECD spectra. The conformations of anomers, α and β, were determined by long selective proton decoupling.

Ginkgetin-KDN-Ac (11R, 11S, 13R, 13S) were prepared from 1 and 8. Ginkgetin-KDN (12R, 12S, 14R, 14S) were prepared from ginkgetin-KDN-Ac (11R, 11S, 13R, 13S) by hydrolysis of the acetyl group with NaOMe, respectively. Sciadopitysin-KDN-Ac (15R, 15S) were prepared from 2 and 8. Sciadopitysin-KDN (16R, 16S) were prepared from biflavonoid and protected sciadopitysin-KDN-Ac (15R, 15S) by hydrolysis of the acetyl group with NaOMe, respectively.

Ginkgetin-GlcNAc-Ac (17R, 17S) were prepared from 1 and 9. Ginkgetin-GlcNAc (18R, 18S) were prepared from ginkgetin-GlcNAc-Ac (17R, 17S) by hydrolysis of the acetyl group with NaOMe, respectively. Sciadopitysin-GlcNAc-Ac (20R, 20S) were prepared from 2 and 9. Sciadopitysin-GlcNAc (21R, 21S) were prepared from sciadopitysin-GlcNAc-Ac (20R, 20S) by hydrolysis of the acetyl group with NaOMe, respectively. Biflavonoid-LacNAc (19R, 19S, 22R, 22S) were prepared from biflavonoid-GlcNAc (18R, 18S, 21R, 21S) respectively, with d-lactose monohydrate (10) as the d-galactose unit donor and β-galactosidase from Bacillus circulans.

![Scheme 1. Synthesis of protected KDN-Ac donor 8](image-url)
Scheme 2. Synthesis of the glycoconjugates of the biflavonoids (1, 2) linked to sugars (3–5)
We found that the sialidase inhibitory activities of the glycoconjugates of biflavonoids (1, 2) and Neu5Ac (6) against sialidase of influenza A virus H1N1 subtype, H3N2 subtype, and influenza B virus were similar to or higher than that of F36 as positive control. The inhibitory activities of the glycoconjugates (12R, 12S, 14R, 14S, 16R, 16S) of biflavonoids (1, 2) and KDN (3) were generally less than that of F36 (Table 1). Therefore, the NHAc moiety of the sialic acid residue is important for the inhibitory activity of biflavonoid-sialic acid glycoconjugates against sialidase of influenza viruses. The glycoconjugates (18R, 18S, 21R, 21S) of biflavonoids (1, 2) and GlcNAc (4) showed selective sialidase inhibitory activity against influenza A H1N1 subtype. In particular, the activity of 18S was similar to or higher than that of F36 (Table 2). The glycoconjugates (19R, 19S, 22R, 22S) of biflavonoids (1, 2) and LacNAc (5) showed little or no activity. These results suggest that the influenza virus sialidase inhibitory activity of the compounds is influenced by the linkage of sugar chains with nitrogen atoms.

**Table 1. Inhibitory activities (IC$_{50}$: µg/mL) against influenza virus sialidase by 11R-16S**

<table>
<thead>
<tr>
<th>Compound</th>
<th>A/New Caledonia/20/99 (H1N1)</th>
<th>A/Guizhou/54/89 (H3N2)</th>
<th>B/Ibaraki/2/85</th>
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<tr>
<td>F36</td>
<td>67.7</td>
<td>82.6</td>
<td>41.6</td>
</tr>
<tr>
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<td>&gt;100.0</td>
<td>&gt;100.0</td>
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<td>&gt;100.0</td>
<td>75.0</td>
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<td>&gt;100.0</td>
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<tr>
<td>15S</td>
<td>&gt;100.0</td>
<td>&gt;100.0</td>
<td>&gt;100.0</td>
</tr>
<tr>
<td>16R</td>
<td>&gt;100.0</td>
<td>85.7</td>
<td>&gt;100.0</td>
</tr>
<tr>
<td>16S</td>
<td>&gt;100.0</td>
<td>&gt;100.0</td>
<td>&gt;100.0</td>
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</table>

**Table 2. Inhibitory activities (IC$_{50}$: µg/mL) against influenza virus sialidase by 17R-22S**

<table>
<thead>
<tr>
<th>Compound</th>
<th>A/New Caledonia/20/99 (H1N1)</th>
<th>A/Hiroshima/52/2005 (H3N2)</th>
<th>B/Ibaraki/2/85</th>
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<tr>
<td>F36</td>
<td>47.4</td>
<td>55.4</td>
<td>27.2</td>
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<tr>
<td>17R</td>
<td>97.1</td>
<td>&gt;100.0</td>
<td>&gt;100.0</td>
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<tr>
<td>17S</td>
<td>&gt;100.0</td>
<td>&gt;100.0</td>
<td>&gt;100.0</td>
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<tr>
<td>18R</td>
<td>69.3</td>
<td>81.6</td>
<td>76.5</td>
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<td>18S</td>
<td>48.5</td>
<td>&gt;100.0</td>
<td>&gt;100.0</td>
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<tr>
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<td>&gt;100.0</td>
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<td>&gt;100.0</td>
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<td>20R</td>
<td>66.8</td>
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<td>20S</td>
<td>59.2</td>
<td>&gt;100.0</td>
<td>&gt;100.0</td>
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<td>&gt;100.0</td>
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<tr>
<td>21S</td>
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<td>94.8</td>
<td>&gt;100.0</td>
</tr>
<tr>
<td>22R</td>
<td>&gt;100.0</td>
<td>&gt;100.0</td>
<td>&gt;100.0</td>
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<tr>
<td>22S</td>
<td>98.0</td>
<td>&gt;100.0</td>
<td>&gt;100.0</td>
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**EXPERIMENTAL**

General Experimental Procedures
Melting points were determined on a Yanaco MP. The IR spectra were recorded with a JASCO IR Report-100 spectrophotometer. UV spectra were recorded with a Shimadzu UV-240 spectrophotometer. Optical rotation was measured with a HORIBA SEPA-300 polarimeter. CD spectra were measured with a Jasco 820 spectropolarimeter. The MS spectra were measured with a JEOL JMS-700 spectrometer. The \(^1\)H- and \(^13\)C- NMR spectra were measured with JEOL JNM-LA500 MHz and JNM-AL400 MHz spectrometers (DMSO-\(d_6\) with TMS). Column chromatography was performed using Kanto Chemical silica gel 60N (63–210 µm), GE Healthcare Sephadex LH-20, and Mitsubishi Chemical DIAION HP-20. HPLC was performed using a Senshu Scientific SSC-346 PUMP measured with a SSC-5410 UV/VIS Detector. Senshu Scientific Senshu Pak PEGASIL-ODS column (5 µm, 20φ × 250 mm). The procedure for the influenza A and B virus sialidase inhibition assay was the same as described previously.\(^2\)

Extraction and isolation
The leaves of *Cephalotaxus harringtonia* K. Koch. var. *harringtonia* were collected in May 2007, in Meiji Pharmaceutical University, Tokyo, Japan. The dried leaves of *C. harringtonia* K. Koch. var. *harringtonia* (1.6 kg) were extracted with CHCl\(_3\) (5 L, 5 times). The concentrated CHCl\(_3\) extract (57 g) was subjected to silica gel column chromatography and eluted with CHCl\(_3\)-MeOH (100:1, 50:1, 30:1, 10:1, 5:1, 3:1, 2:1, 1:1), to afford seven fractions (G1–G7). Fraction G2 (15.4 g) was precipitated and filtered with CHCl\(_3\)-MeOH (10:1), isolating 1 (1.8 g, 3.2 mmol) as a solid.\(^8\) The leaves of *Sciadopitys verticillata* Sieb. Et Zucc. were collected in April 2007, in Meiji Pharmaceutical University, Tokyo, Japan. The dried leaves of *S. verticillata* Sieb. Et Zucc. (1.3 kg) were extracted with CHCl\(_3\) (5 L, 4 times). The concentrated CHCl\(_3\) extract (94.1 g) was subjected to silica gel column chromatography and eluted with CHCl\(_3\)-MeOH (100:1, 50:1, 30:1, 10:1, 5:1, 3:1, 2:1, 1:1) to afford seven fractions (S1–S7). Fraction S2 (44.6 g) was precipitated and filtered with CHCl\(_3\)-MeOH (10:1), isolating 2 (5.9 g, 10 mmol) as a solid.\(^8\)

General procedure for the preparation of 8 from 7
To a solution of 7 (1.05 g, 2.13 mmol) in 1 M HCl-AcOH (10.5 mL) was added AcCl (1.05 mL) and stirred at rt under Ar gas in the dark for 48 h. Then the solution was concentrated and separated with water and CHCl\(_3\). The organic layer was dried over anhydrous sodium sulfate and concentrated to afford 8 (971.1 mg, 89.1%).\(^5\)
General procedure for the preparation of 11R, 11S, 13R, and 13S from 1 and 8
A solution of 1 (200.9 mg, 355 µmol) and NaH (42 mg, 1.8 mmol) in dry DMF (9.0 mL) was stirred at rt under Ar gas in the dark. After stirring the reaction mixture for 1 h, 8 (400.2 mg, 783 µmol) was added, and the mixture stirred for 18 h at rt under Ar gas in the dark. Then the solution was separated with water and CHCl₃. The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. The residue was purified by Sephadex LH-20 column chromatography and eluted with MeOH and HPLC (toluene-acetone (13:2), hexane-acetone (2:1), hexane-acetone (4:3)) to afford 11R (7.2 mg, 6.9 µmol, 2.0%), 11S (18.8 mg, 18.1 µmol, 5.1%), 13R (36.0 mg, 23.8 µmol, 6.7%), and 13S (63.5 mg, 41.9 µmol, 11.9%).

(R)-7',4'-Di-O-methyl-7"-O-(methyl 4,5,7,8,9-penta-O-acetyl-3-deoxy-D-glycero-D-galacto-2-nonulopyranosyloate)amentoflavone (11R)
Yellow powder; mp 154–157 °C; \([\alpha]_D^{26} \, +5.8 \) (c 0.40, MeOH); IR \(\nu_{\text{max}}\) (KBr) cm\(^{-1}\): 3425, 2945, 1745, 1650, 1600, 1500, 1440, 1370, 1220, 1055, 835; UV \(\lambda_{\text{max}}\) (MeOH) nm (log \(\varepsilon\)): 207 (4.70), 270 (4.55), 330 (4.54); CD \(\lambda_{\text{max}}\) (MeOH) nm (\([\theta]^{25}\)) - 337 (-100774), 307 (+48754), 286 (+9999), 264 (+467056), 239 (-9917); FAB-MS (positive) m/z: 1041 ([M+H]+), 567, 535; HR-FAB-MS (positive) m/z: 1041.2672 [M+H]+ (calcd for 1041.2665, C₅₂H₄₉O₂₃); \(^1\)H-NMR (DMSO-d₆) see Table S1; \(^1^3\)C-NMR (DMSO-d₆) see Table S7.

(S)-7',4'-Di-O-methyl-7"-O-(methyl 4,5,7,8,9-penta-O-acetyl-3-deoxy-D-glycero-D-galacto-2-nonulopyranosyloate)amentoflavone (11S)
Yellow powder; mp 154–156 °C; \([\alpha]_D^{26} \, +33.8 \) (c 0.38, MeOH); IR \(\nu_{\text{max}}\) (KBr) cm\(^{-1}\): 3425, 2950, 1745, 1650, 1600, 1500, 1440, 1370, 1215, 1055, 840; UV \(\lambda_{\text{max}}\) (MeOH) nm (log \(\varepsilon\)): 207 (4.84), 268 (4.63), 330 (4.63); CD \(\lambda_{\text{max}}\) (MeOH) nm (\([\theta]^{25}\)) - 336 (+195086), 307 (-133693), 284 (+7153), 264 (-41552), 241 (+10271); FAB-MS (positive) m/z: 1041 ([M+H]+), 567, 535; HR-FAB-MS (positive) m/z: 1041.2660 [M+H]+ (calcd for 1041.2665, C₅₂H₄₉O₂₃); \(^1\)H-NMR (DMSO-d₆) see Table S1; \(^1^3\)C-NMR (DMSO-d₆) see Table S7.

(R)-7',4''-Di-O-methyl-7"",4""-di-O-(methyl 4,5,7,8,9-penta-O-acetyl-3-deoxy-D-glycero-D-galacto-2-nonulopyranosyloate)amentoflavone (13R)
Yellow powder; mp 132–134 °C; \([\alpha]_D^{26} \, -59.0 \) (c 0.50, MeOH); IR \(\nu_{\text{max}}\) (KBr) cm\(^{-1}\): 3425, 2950, 1750, 1650, 1600, 1500, 1425, 1370, 1220, 1155, 840; UV \(\lambda_{\text{max}}\) (MeOH) nm (log \(\varepsilon\)): 207 (4.84), 271 (4.72), 319 (4.64); CD \(\lambda_{\text{max}}\) (MeOH) nm (\([\theta]^{25}\)) - 329 (-118591), 302 (+42879), 285 (+14479), 267 (+70125), 238 (-26079); FAB-MS (positive) m/z: 1515 ([M+H]+), 1041, 567, 535; HR-FAB-MS (positive) m/z:
1515.4036 [M+H]^+ (calcd for 1515.4038, C_{72}H_{75}O_{36}); ^1H-NMR (DMSO-d_6) see Table S2; ^13C-NMR (DMSO-d_6) see Table S7.

(S)-7,4''-Di-O-methyl-7''',4'''-di-O-(methyl 4,5,7,8,9-penta-O-acetyl-3-deoxy-D-glycero-D-galacto-2-nonulopyranosyloate)amentoflavone (13S)
Yellow powder; mp 135–138 °C; [α]_D^{25} +31.3 (c 0.50, MeOH); IR ν_{max} (KBr) cm^{-1}: 3450, 2960, 1650, 1605, 1500, 1435, 1370, 1220, 1050, 840; UV λ_{max} (MeOH) nm (log ε): 204 (5.00), 270 (4.82), 318 (4.75); CD λ_{max} (MeOH) nm ([θ]_D^{25}): 370 (−106438), 331 (+117521), 303 (−61940), 283 (+181179), 266 (−30146), 245 (−11542), 232 (−46216); FAB-MS (positive) m/z: 1515 [M+H]^+ (calcd for 1515.4038, C_{72}H_{75}O_{36}); ^1H-NMR (DMSO-d_6) see Table S2; ^13C-NMR (DMSO-d_6) see Table S7.

General procedure for the preparation of 12R from 11R
To a solution of 11R (17.7 mg, 17.0 µmol) in MeOH (2.0 mL) was added 28% NaOMe MeOH solution (2.0 mL) and stirred at rt for 5 h under Ar gas in the dark. Then H_2O (4.0 mL) was added and stirred for 18 h at rt. The reaction mixture was treated with 2 M HCl, and the solution was concentrated in vacuo. The residue was purified by column chromatography on a DIAION HP-20 (H_2O, MeOH) to afford 12R (13.1 mg, 16.0 µmol, 94.3%).

(R)-7,4'-Di-O-methyl-7''-O-(methyl 3-deoxy-D-glycero-D-galacto-2-nonulopyranosyloate)amentoflavone (12R)
Yellow powder; mp 216 °C (dec.); [α]_D^{24} −44.0 (c 0.40, MeOH); IR ν_{max} (KBr) cm^{-1}: 3420, 2875, 1650, 1500, 1460, 1090, 800; UV λ_{max} (MeOH) nm (log ε): 207 (4.75), 271 (4.61), 333 (4.60); CD λ_{max} (MeOH) nm ([θ]_D^{25}): 379 (+9679), 338 (−190832), 308 (+111102), 286 (+6022), 268 (+71838), 243 (+5079); FAB-MS (negative) m/z: 815 ([M−H]^−) (calcd for 815.1823, C_{41}H_{35}O_{18}); ^1H-NMR (CD_3OD) see Table S1.

General procedure for the preparation of 12S from 11S
To a solution of 11S (15.9 mg, 15.3 µmol) in MeOH (2.0 mL) was added 28% NaOMe MeOH solution (2.0 mL) and stirred at rt for 5 h under Ar gas in the dark. Then H_2O (4.0 mL) was added and stirred for 18 h at rt. The reaction mixture was treated with 2 M HCl, and the solution was concentrated in vacuo. The residue was purified by column chromatography on a DIAION HP-20 (H_2O, MeOH) to afford 12S (11.9 mg, 14.6 µmol, 95.4%).
(S)-7,4'-Di-O-methyl-7''-O-(methyl 3-deoxy-D-glycero-D-galacto-2-nonulopyranosyloate)amentoflavone (12S)

Yellow powder; mp 225–226 °C (dec.); [α]D23 +70.6 (c 0.35, MeOH); IR vmax (KBr) cm⁻¹: 3425, 1690, 1650, 1600, 1380, 1040, 900, 830; UV λmax (MeOH) nm (log ε): 206 (4.67), 270 (4.54), 331 (4.53); CD λmax (MeOH) nm ([θ]23): 373 (−6228), 337 (+167891), 308 (−91297), 286 (+3144), 268 (−51294), 242 (+3193); FAB-MS (negative) m/z: 815 [M−H]−, 565, 513, 467, 459; HR-FAB-MS (negative) m/z: 815.1835 [M−H]− (calcd for 815.1823, C41H35O18);

1H-NMR (CD3OD) see Table S1.

General procedure for the preparation of 14R from 13R

To a solution of 13R (19.7 mg, 13.0 µmol) in MeOH (2.0 mL) was added 28% NaOMe MeOH solution (2.0 mL) and stirred at rt for 5 h under Ar gas in the dark. Then H2O (4.0 mL) was added and stirred for 18 h at rt. The reaction mixture was treated with 2 M HCl, and the solution was concentrated in vacuo. The residue was purified by column chromatography on a DIAION HP-20 (H2O, MeOH) to afford 14R (14.9 mg, 14.0 µmol, 107%).

(R)-7,4'-Di-O-methyl-7''-O-(methyl 3-deoxy-D-glycero-D-galacto-2-nonulopyranosyloate)amentoflavone (14R)

Yellow powder; mp 221–224 °C (dec.); [α]D24 +41.7 (c 0.33, MeOH); IR vmax (KBr) cm⁻¹: 3420, 1710, 1610, 1500, 1430, 1340, 1050, 840; UV λmax (MeOH) nm (log ε): 207 (4.68), 272 (4.68), 327 (4.50); CD λmax (MeOH) nm ([θ]25): 371 (+11473), 335 (−103964), 306 (+58402), 286 (+980), 268 (+46498), 243 (−2252); FAB-MS (positive) m/z: 1089 [M+Na]+, 861, 839, 567, 505; HR-FAB-MS (positive) m/z: 1089.2494 [M+Na]+ (calcd for 1089.2488, C50H50O26Na);

1H-NMR (CD3OD) see Table S2.

General procedure for the preparation of 14S from 13S

To a solution of 13S (22.0 mg, 14.5 µmol) in MeOH (2.0 mL) was added 28% NaOMe MeOH solution (2.0 mL) and stirred at rt for 5 h under Ar gas in the dark. Then H2O (4.0 mL) was added and stirred for 18 h at rt. The reaction mixture was treated with 2 M HCl, and the solution was concentrated in vacuo. The residue was purified by column chromatography on a DIAION HP-20 (H2O, MeOH) to afford 14S (12.3 mg, 12.3 µmol, 79.4%).

(S)-7,4'-Di-O-methyl-7''-O-(methyl 3-deoxy-D-glycero-D-galacto-2-nonulopyranosyloate)amentoflavone (14S)
Yellow powder; mp 229–231 °C (dec.); \([\alpha]_D^{25} \) −46.6 (c 0.40, MeOH); IR \(\nu_{\text{max}}\) (KBr) cm\(^{-1}\): 3440, 2940, 1610, 1500, 1450, 1340, 1065, 820; UV \(\lambda_{\text{max}}\) (MeOH) nm (log \(\varepsilon\)): 206 (4.73), 272 (4.60), 328 (4.57); CD \(\lambda_{\text{max}}\) (MeOH) nm (\([\theta]_D^{25}\)): 370 (−15517), 334 (+132796), 306 (−57096), 286 (+12198), 269 (−36196), 255 (−14854), 250 (−16933), 244 (−12588), 228 (−86169); FAB-MS (positive) \(m/z\): 1089 (\([\text{M+Na}]^+\)), 861, 839, 612, 567, 551; HR-FAB-MS (positive) \(m/z\): 1089.2479 (calcd for 1089.2488, C\(_{50}\)H\(_{50}\)O\(_{26}\)Na); \(^1\)H-NMR (CD\(_3\)OD) see Table S2.

General procedure for the preparation of 15R and 15S from 2 and 8

A solution of 2 (120.3 mg, 207 \(\mu\)mol) and NaH (20.1 mg, 838 \(\mu\)mol) in dry DMF (6.0 mL) was stirred at rt under Ar gas in the dark. After stirring the reaction mixture for 1 h, 8 (251.9 mg, 493 \(\mu\)mol) was added, and the mixture stirred for 18 h at rt under Ar gas in the dark. Then the solution was separated with water and CHCl\(_3\). The organic layer was dried over anhydrous sodium sulfate and concentrated \textit{in vacuo}. The residue was purified by Sephadex LH-20 column chromatography and eluted with MeOH and HPLC (toluene-acetone (13:2), hexane-acetone (2:1), hexane-acetone (4:3)) to afford 15R (18.1 mg, 17.2 \(\mu\)mol, 8.3%) and 15S (21.2 mg, 20.1 \(\mu\)mol, 9.7%).

\((R)-7,4',4'''-\text{Tri-O-methyl-7-''''O-(methyl 4,5,7,8,9-penta-O-acetyl-3-deoxy-D-glycero-D-galacto-2-nonenulopyranosyloate)}\)amentoflavone (15R)

Yellow powder; mp 146–148 °C; \([\alpha]_D^{30} \) −64.9 (c 0.50, MeOH); IR \(\nu_{\text{max}}\) (KBr) cm\(^{-1}\): 3450, 2960, 1750, 1655, 1605, 1510, 1430, 1370, 1260, 1160, 1040, 840; UV \(\lambda_{\text{max}}\) (MeOH) nm (log \(\varepsilon\)): 207 (4.81), 270 (4.63), 328 (4.62); CD \(\lambda_{\text{max}}\) (MeOH) nm (\([\theta]_D^{25}\)): 334.4 (−95421), 306 (+40755), 285 (+11507), 265 (+44213), 240 (−9651); FAB-MS (positive) \(m/z\): 1055 ([M+H]+), 1013, 581, 580, 549; HR-FAB-MS (positive) \(m/z\): 1055.2823 ([M+H]+) (calcd for 1055.2821, C\(_{53}\)H\(_{51}\)O\(_{23}\)); \(^1\)H-NMR (DMSO-\(d_6\)) see Table S3; \(^{13}\)C-NMR (DMSO-\(d_6\)) see Table S7.

\((S)-7,4',4'''-\text{Tri-O-methyl-7-''''O-(methyl 4,5,7,8,9-penta-O-acetyl-3-deoxy-D-glycero-D-galacto-2-nonenulopyranosyloate)}\)amentoflavone (15S)

Yellow powder; mp 149–151 °C; \([\alpha]_D^{30} \) +37.6 (c 0.50, MeOH); IR \(\nu_{\text{max}}\) (KBr) cm\(^{-1}\): 3450, 2950, 1750, 1650, 1600, 1500, 1425, 1365, 1210, 1160, 1050, 835; UV \(\lambda_{\text{max}}\) (MeOH) nm (log \(\varepsilon\)): 206 (4.83), 269 (4.61), 329 (4.60); CD \(\lambda_{\text{max}}\) (MeOH) nm (\([\theta]_D^{25}\)): 372 (−4916), 335 (+74438), 307 (−51304), 284 (+2372), 267 (−15243), 242 (+4199), 228 (−29176); FAB-MS (positive) \(m/z\): 1055 ([M+H]+), 1013, 581, 580, 549; HR-FAB-MS (positive) \(m/z\): 1055.2825 ([M+H]+) (calcd for 1055.2821, C\(_{53}\)H\(_{51}\)O\(_{23}\)); \(^1\)H-NMR (DMSO-\(d_6\)) see Table S3; \(^{13}\)C-NMR (DMSO-\(d_6\)) see Table S7.
General procedure for the preparation of **16R** from **15R**

A solution of **15R** (41.8 mg, 39.6 µmol) and MeOH (4.0 mL) was added 28% NaOMe MeOH solution (4.0 mL) and stirred at rt for 5 h under Ar gas in the dark. Then H₂O (4.0 mL) was added and stirred for 18 h at rt. The reaction mixture was treated with 2M HCl and concentrated in vacuo. The residue was purified by column chromatography on DIAION HP-20 (H₂O → MeOH) to afford **16R** (28.3 mg, 34.1 µmol, 86%).

(R)-7,4′,4″-Tri-O-methyl-7″-O-(methyl 3-deoxy-D-glycero-D-galacto-2-nonulopyranosyloate)amentoflavone (**16R**)

Yellow powder; mp 220 ℃ (dec.); [α]D²⁴ +17.8 (c 0.44, MeOH); IR νmax (KBr) cm⁻¹: 3405, 1680, 1610, 1500, 1040, 830; UV λmax (MeOH) nm (log ε): 206 (4.57), 271 (4.43), 328 (4.42); CD λmax (MeOH) nm ([θ]²⁵): 376 (+5670), 337 (−96846), 307 (+54208), 286 (+2868), 268 (+36437), 243 (+129); FAB-MS (positive) m/z: 831 ([M+H]+), 581, 580, 549; HR-FAB-MS (positive) m/z: 831.2131 [M+H]+ (calcd for 831.2136, C₄₂H₃₉O₁₈); ¹H-NMR (CD₃OD) see S3.

General procedure for the preparation of **16S** from **15S**

A solution of **15S** (36.1 mg, 34.2 µmol) and MeOH (3.5 mL) was added 28% NaOMe MeOH solution (3.5 mL) and stirred at rt for 5 h under Ar gas in the dark. Then H₂O (7 mL) was added and stirred for 18 h at rt. The reaction mixture was treated with 2M HCl and concentrated in vacuo. The residue was purified by column chromatography on DIAION HP-20 (H₂O → MeOH) to afford **16S** (14.1 mg, 17.0 µmol, 49.6%).

(S)-7,4′,4″-Tri-O-methyl-7″-O-(methyl 3-deoxy-D-glycero-D-galacto-2-nonulopyranosyloate)amentoflavone (**16S**)

Yellow powder; mp 205-206 ℃ (dec.); [α]D²⁶ −13.6 (c 0.44, MeOH); IR νmax (KBr) cm⁻¹: 3425, 2875, 1640, 1520, 1415, 1120, 1030, 830; UV λmax (MeOH) nm (log ε): 206 (4.51), 271 (4.38), 328 (4.37); CD λmax (MeOH) nm ([θ]²⁵): 374 (−6071), 336 (+9168), 307 (−48573), 286 (+2315), 269 (−29096), 243 (+2064); FAB-MS (positive) m/z: 831 ([M+H]+), 581, 580, 549; HR-FAB-MS (positive) m/z: 831.2139 [M+H]+ (calcd for 831.2136, C₄₂H₃₉O₁₈); ¹H-NMR (CD₃OD) see S3.

General procedure for the preparation of **17R** and **17S** from **1** and **9**

A solution of **1** (1.00 g, 1.77 mmol) and NaH (86.4 mg, 3.60 mmol) in dry DMF (20 mL) was stirred at rt under Ar gas in the dark. After stirring the reaction mixture for 1 h, **9** (1.50 g, 4.10 mmol) was added, and the mixture stirred for 18 h at rt under Ar gas in the dark. The solution was diluted with water and CHCl₃. The organic layer was separated and dried over anhydrous sodium sulfate. After the CHCl₃ layer was
evaporated, the residue was purified by Sephadex LH-20 column chromatography and eluted with MeOH and normal-phase HPLC (toluene-acetone (3:2) to afford 17R (161.4 mg, 180.2 µmol, 10.2%) and 17S (213.7 mg, 238.6 µmol, 13.5%).

(R)-7,4'-Di-O-methyl-7''-O-(3,4,6-tri-O-acetyl-2-acetamide-2-deoxy-α-glucopyranosyl)amentoflavone (17R)

Yellow powder; mp 174–176 °C; [α]D22 −4.6 (c 0.50, MeOH); IR νmax (KBr) cm⁻¹: 3425, 2950, 1750, 1650, 1600, 1500, 1440, 1370, 1240, 1040, 840; UV λmax (MeOH) nm (log e): 207 (4.82), 270 (4.66), 331 (4.66); CD λmax (MeOH) nm ([θ]25⁰): 338 (−145766), 307 (+64967), 285 (−14603), 265 (+64994), 239 (−18527); FAB-MS (positive) m/z: 896 ([M+H]+), 567, 535; HR-FAB-MS (positive) m/z: 896.2407 [M+H]+ (calcd for 896.2402, C46H42NO18); ¹H-NMR (DMSO-d6) see Table S4; ¹³C-NMR (DMSO-d6) see Table S8.

(S)-7,4'-Di-O-methyl-7''-O-(3,4,6-tri-O-acetamido-2-deoxy-α-glucopyranosyl)amentoflavone (17S)

Yellow powder; mp 176–177 °C; [α]D22 +38.2 (c 0.50, MeOH); IR νmax (KBr) cm⁻¹: 3450, 1730, 1640, 1570, 1500, 1230, 1160, 1050, 820; UV λmax (MeOH) nm (log e): 207 (4.76), 270 (4.60), 332 (4.60); CD λmax (MeOH) nm ([θ]25⁰): 335 (+101834), 306 (−38800), 283 (+12716), 264 (−12108), 239 (−30367); FAB-MS (positive) m/z: 896 ([M+H]+), 567, 551, 330; HR-FAB-MS (positive) m/z: 896.2397 [M+H]+ (calcd for 896.2402, C46H42NO18); ¹H-NMR (DMSO-d6) see Table S4; ¹³C-NMR (DMSO-d6) see Table S8.

General procedure for the preparation of 18R from 17R

To a solution of 17R (115.0 mg, 128 µmol) and MeOH (10 mL) was added 28% NaOMe MeOH solution (10 mL) and stirred at rt for 5 h under Ar gas in the dark. Then H2O (10 mL) was added and stirred for 18 h at rt. The reaction mixture was treated with 2 M HCl and concentrated in vacuo. The residue was precipitated and filtered with H2O to afford 18R (97.0 mg, 126 µmol, 98.2%) as a solid.

(R)-7,4'-Di-O-methyl-7''-O-(2-acetamide-2-deoxy-α-glucopyranosyl)amentoflavone (18R)

Yellow powder; mp 202–204 °C; [α]D21 −27.4 (c 0.50, MeOH); IR νmax (KBr) cm⁻¹: 3350, 1650, 1600, 1440, 1340, 1250, 1160, 1080, 830; UV λmax (MeOH) nm (log e): 205 (4.67), 270 (4.51), 329 (4.51); CD λmax (MeOH) nm ([θ]25⁰): 338 (−106996), 307 (+47241), 286 (+11879), 264 (+49444), 239 (−12053); FAB-MS (positive) m/z: 770 ([M+H]+), 567; HR-FAB-MS (positive) m/z: 770.2083 [M+H]+ (calcd for 770.2085, C40H36NO15); ¹H-NMR (DMSO-d6) see Table S4; ¹³C-NMR (DMSO-d6) see Table S8.
General procedure for the preparation of **18S** from **17S**

To a solution of **17S** (98.0 mg, 109 µmol) and MeOH (10 mL) was added 28% NaOMe MeOH solution (10 mL) and stirred at rt for 5 h under Ar gas in the dark. Then H₂O (10 mL) was added and stirred for 18 h at rt. The reaction mixture was treated with 2 M HCl and concentrated *in vacuo*. The residue was precipitated and filtered with H₂O to afford **18S** (77.5 mg, 101 µmol, 92.0%) as solid.

**(S)-7,4'-Di-O-methyl-7''-O-(2-acetamide-2-deoxy-D-glucopyranosyl)amentoflavone (18S)**

Yellow powder; mp 199 °C; [α]D^22 +3.3 (c 0.50, MeOH); IR ν<sub>max</sub> (KBr) cm<sup>−1</sup>: 3375, 2810, 1640, 1500, 1160, 1040, 840; UV λ<sub>max</sub> (MeOH) nm (log ε): 206 (4.74), 270 (4.58), 331 (4.58); CD λ<sub>max</sub> (MeOH) nm ([θ]25): 374 (−2667), 335 (+80748), 307 (−50803), 284 (−3458), 264 (−23556), 241 (+8662); FAB-MS (positive) m/z: 770 ([M+H]^+), 567; HR-FAB-MS (positive) m/z: 770.2085 [M+H]^+ (calcd for 770.2085, C<sub>40</sub>H<sub>36</sub>N<sub>15</sub>O<sub>15</sub>);

General procedure for the preparation of **19R** from **18R**

To a solution of **18R** (99.1 mg, 129 µmol) and **10** (800 mg, 2.22 mmol) in 100 mM phosphate buffer (20 mL, pH 7.4) and MeCN (20 mL) was added *B. circulans* β-galactosidase (0.5 mg, 6 U) and incubated for 18 h at 30 °C in the dark. The reaction was terminated by heating for 5 min at 100 °C. The concentrated reaction mixture was purified by normal-phase HPLC (CHCl<sub>3</sub>-MeOH (7:2)) to afford **19R** (13.5 mg, 14.5 µmol, 11.3%).

**(R)-7,4'-Di-O-methyl-7''-O-(2-acetamide-2-deoxy-4-O-(β-galactopyranosyl)-D-glucopyranosyl)amentoflavone (19R)**

Yellow powder; mp 208–210 °C; [α]D^23 +88.2 (c 0.50, MeOH); IR ν<sub>max</sub> (KBr) cm<sup>−1</sup>: 3400, 2850, 1650, 1600, 1500, 1070, 820; UV λ<sub>max</sub> (MeOH) nm (log ε): 206 (4.62), 270 (4.45), 331 (4.45); CD λ<sub>max</sub> (MeOH) nm ([θ]25): 338 (−94442), 307 (+44811), 286 (+10808), 265 (+44845), 239 (−11147); FAB-MS (positive) m/z: 932 ([M+H]^+), 567, 535; HR-FAB-MS (positive) m/z: 932.2614 [M+H]^+ (calcd for 932.2613, C<sub>46</sub>H<sub>46</sub>N<sub>20</sub>O<sub>20</sub>); **1**H-NMR (DMSO-<i>d</i><sub>6</sub>) see Table S6; **13**C-NMR (DMSO-<i>d</i><sub>6</sub>) see Table S8.

General procedure for the preparation of **19S** from **18S**

To a solution of **18S** (85.7 mg, 111 µmol) and **10** (800 mg, 2.22 mmol) in 100 mM phosphate buffer (20 mL, pH 7.4) and MeCN (20 mL) was added *B. circulans* β-galactosidase (0.5 mg, 6 U) and incubated for 18 h at 30 °C in the dark. The reaction was terminated by heating for 5 min at 100 °C. The concentrated
reaction mixture was purified by normal-phase HPLC (CHCl₃-MeOH (7:2)) to afford **19S** (9.5 mg, 10.2 µmol, 9.2%).

(S)-7,4'-Di-O-methyl-7''-O-(2-acetamide-2-deoxy-4-O-(β-galactopyranosyl)-D-glucopyranosyl)amentoflavone (**19S**)

Yellow powder; mp 204–206 °C; [α]D⁰⁻⁵₆.₈ (c 0.50, MeOH); IR νmax (KBr) cm⁻¹: 3425, 1650, 1550, 1070, 820; UV λmax (MeOH) nm (log ε): 206 (4.76), 270 (4.60), 332 (4.62); CD λmax (MeOH) nm ([θ]D²⁵): 373 (−1224), 335 (+78978), 307 (−47866), 283 (−3343), 265 (−26246), 240 (+6047); FAB-MS (positive) m/z: 932 ([M+H]+), 567, 535; HR-FAB-MS (positive) m/z: 932.2609 [M+H]+ (calcd for 932.2613, C₄₆H₄₆N₂O₂₀); ¹H-NMR (DMSO-d₆) see Table S6; ¹³C-NMR (DMSO-d₆) see Table S8.

General procedure for the preparation of **20R** and **20S** from **2** and **9**

A solution of **2** (1.0 g, 1.72 mmol) and NaH (100 mg, 4.2 mmol) in dry DMF (24 mL) was stirred at rt under Ar gas in the dark. After stirring the reaction mixture for 1 h, **9** (1.50 g, 4.10 mmol) was added, and the mixture stirred for 18 h at rt under Ar gas in the dark. The solution was diluted with water and CHCl₃. The organic layer was separated and dried over anhydrous sodium sulfate. After the CHCl₃ layer was evaporated, the residue was purified by Sephadex LH-20 column chromatography and eluted with MeOH and silica gel C. C. (toluene-acetone (10: 1, 5: 1, 3: 1, 2: 1, 1: 1) to afford **20R** (170.1 mg, 187 µmol, 10.9%), **20S** (205.7 mg, 226 µmol, 13.1%).

(R)-7,4',4''-Tri-O-methyl-7''-O-(3,4,6-tri-O-acetyl-2-acetamide-2-deoxy-D-glucopyranosyl)amentoflavone (**20R**)

Yellow powder; mp 157–158 °C; [α]D²⁶⁺₅₇.₆ (c 1.0, MeOH); IR νmax (KBr) cm⁻¹: 3400, 2960, 1740, 1650, 1600, 1500, 1440, 1360, 1240, 1040, 835; UV λmax (MeOH) nm (log ε): 207 (4.93), 270 (4.78), 327 (4.77); CD λmax (MeOH) nm ([θ]D²⁵): 335 (−211258), 306 (+92372), 285 (+23917), 264 (+92372), 239 (−26732), 224 (+16427); FAB-MS (positive) m/z: 910 ([M+H]+), 582, 581, 549; HR-FAB-MS (positive) m/z: 910.2564 [M+H]+ (calcd for 910.2558, C₄₇H₄₄NO₁₈); ¹H-NMR (DMSO-d₆) see Table S5; ¹³C-NMR (DMSO-d₆) see Table S8.

(S)-7,4',4''-Tri-O-methyl-7''-O-(3,4,6-tri-O-acetyl-2-acetamide-2-deoxy-D-glucopyranosyl)amentoflavone (**20S**)

Yellow powder; mp 160–161 °C; [α]D²⁷⁻₈.₆ (c 1.0, MeOH); IR νmax (KBr) cm⁻¹: 3420, 2940, 1750, 1650, 1600, 1500, 1430, 1360, 1240, 1040, 830; UV λmax (MeOH) nm (log ε): 207 (4.67), 270 (4.53), 328 (4.52);
CD \( \lambda_{\text{max}} \) (MeOH) nm ([\( \Theta \)]{sub}25): 334 (+64447), 305 (−42296), 283 (−5824), 266 (−23068), 240 (+7528), 228 (−12362); FAB-MS (positive) \( m/z \): 910 ([M+H]{sup}+), 582, 581, 549; HR-FAB-MS (positive) \( m/z \): 910.2556 [M+H]{sup}+ (calcd for 910.2558, C_{47}H_{44}NO_{18}); \(^1\)H-NMR (DMSO-\( d_6 \)) see Table S5; \(^1^3\)C-NMR (DMSO-\( d_6 \)) see Table S8.

General procedure for the preparation of 21R from 20R

To a solution of 20S (40.8 mg, 45 \( \mu \)mol) and MeOH (10 mL) was added 28\% NaOMe MeOH solution (10 mL) and stirred at rt for 5 h under Ar gas in the dark. Then H\(_2\)O (10 mL) was added and stirred for 18 h at rt. The reaction mixture was treated with 2 M HCl and concentrated in vacuo. The residue was precipitated and filtered with H\(_2\)O to afford 21R (36.3 mg, 46 \( \mu \)mol, 103\%) as solid.

(R)-7,4',4''-Tri-O-methyl-7''-O-(2-acetamide-2-deoxy-d-glucopyranosyl)amentoflavone (21R)

Yellow powder; mp 161–162 °C; [\( \alpha \)]{sub}D\(_{27}\) +52.3 (c 0.30, MeOH); IR \( \nu_{\text{max}} \) (KBr) cm\(^{-1}\): 3400, 1650, 1600, 1560, 1500, 1420, 1260, 1160, 1020, 835; UV \( \lambda_{\text{max}} \) (MeOH) nm (log \( \varepsilon \)): 205 (4.89), 271 (4.74), 326 (4.73); CD \( \lambda_{\text{max}} \) (MeOH) nm ([\( \Theta \)]{sub}25): 337 (−188895), 306 (+80907), 285 (+24235), 264 (+86522), 239 (−22585), 223 (+13347); FAB-MS (positive) \( m/z \): 784 ([M+H]{sup}+), 581, 580, 549; HR-FAB-MS (positive) \( m/z \): 784.2242 [M+H]{sup}+ (calcd for 784.2241, C_{41}H_{38}NO_{15}); \(^1\)H-NMR (DMSO-\( d_6 \)) see Table S5; \(^1^3\)C-NMR (DMSO-\( d_6 \)) see Table S8.

General procedure for the preparation of 21S from 20S

To a solution of 20S (40.0 mg, 44 mmol) and MeOH (10 mL) was added 28\% NaOMe MeOH solution (10 mL) and stirred at rt for 5 h under Ar gas in the dark. Then H\(_2\)O (10 mL) was added and stirred for 18 h at rt. The reaction mixture was treated with 2 M HCl and concentrated in vacuo. The residue was precipitated and filtered with H\(_2\)O to afford 21S (35.6 mg, 46 \( \mu \)mol, 103\%) as solid.

(S)-7,4',4''-Tri-O-methyl-7''-O-(2-acetamide-2-deoxy-d-glucopyranosyl)amentoflavone (21S)

Yellow powder; mp 164–166 °C; [\( \alpha \)]{sub}D\(_{22}\) +11.6 (c 0.30, MeOH); IR \( \nu_{\text{max}} \) (KBr) cm\(^{-1}\): 3400, 2950, 1650, 1600, 1500, 1420, 1320, 1250, 1160, 1020, 830; UV \( \lambda_{\text{max}} \) (MeOH) nm (log \( \varepsilon \)): 206 (4.76), 270 (4.61), 328 (4.60); CD \( \lambda_{\text{max}} \) (MeOH) nm ([\( \Theta \)]{sub}25): 334 (+81983), 306 (−52054), 283 (−4148), 264 (−23635), 240 (+10202), 227 (−14657); FAB-MS (positive) \( m/z \): 784 ([M+H]{sup}+), 581, 580, 549; HR-FAB-MS (positive) \( m/z \): 784.2245 [M+H]{sup}+ (calcd for 784.2241, C_{41}H_{38}NO_{15}); \(^1\)H-NMR (DMSO-\( d_6 \)) see Table S5; \(^1^3\)C-NMR (DMSO-\( d_6 \)) see Table S8.

General procedure for the preparation of 22R from 21R
To a solution of 21R (172.6 mg, 220 µmol) and 10 (1.5 g, 4.2 mmol) in 100 mM phosphate buffer (30 mL, pH 7.4) and MeCN (30 mL) was added *B. circulans* β-galactosidase (1.0 mg, 12 U) and incubated for 18 h at 30 °C in the dark. The reaction was terminated by heating for 5 min at 100 °C. The concentrated reaction mixture was purified by normal-phase HPLC (CHCl₃-MeOH (5: 1)) to afford 22R (27.4 mg, 29 µmol, 13.2%).

(R)-7,4',4''-Tri-O-methyl-7''-O-(2-acetamide-2-deoxy-4-O-(β-galactopyranosyl)-d-glucopyranosyl)-amentoflavone (22R)

Yellow powder; mp 180 °C; [α]D²⁶ +16.4 (c 0.50, MeOH); IR ν_max (KBr) cm⁻¹: 3375, 1650, 1490, 1440, 1370, 1260, 1160, 1020, 840; UV λ_max (MeOH) nm (log ε): 207 (4.86), 270 (4.69), 327 (4.69); CD λ_max (MeOH) nm ([θ]: 335 (−29648), 306 (+106465), 285 (+32377), 265 (+110225), 239 (−25742); FAB-MS (positive) m/z: 946 ([M+H]+), 581, 580, 549, 505, 366; HR-FAB-MS (positive) m/z: 946.2766 [M+H]+ (calcd for 946.2770, C₄₇H₄₈NO₂₀);

1H-NMR (DMSO-d₆) see Table S6; 13C-NMR (DMSO-d₆) see Table S8.

General procedure for the preparation of 22S from 21S

To a solution of 21S (183.6 mg, 234 µmol) and 10 (1.5 g, 4.2 mmol) in 100 mM phosphate buffer (30 mL, pH 7.4) and MeCN (30 mL) was added *B. circulans* β-galactosidase (1.0 mg, 12 U) and incubated for 18 h at 30 °C in the dark. The reaction was terminated by heating for 5 min at 100 °C. The concentrated reaction mixture was purified by normal-phase HPLC (CHCl₃-MeOH (5: 1)) to afford 22R (20.4 mg, 20 µmol, 9.2%).

(S)-7,4',4''-Tri-O-methyl-7''-O-(2-acetamide-2-deoxy-4-O-(β-galactopyranosyl)-d-glucopyranosyl)-amentoflavone (22S)

Yellow powder; mp 184–185 °C; [α]D²⁷ +0.4 (c 0.50, MeOH); IR ν_max (KBr) cm⁻¹: 3440, 2925, 1650, 1600, 1500, 1440, 1250, 1160, 1060, 840; UV λ_max (MeOH) nm (log ε): 207 (4.66), 270 (4.49), 329 (4.48); CD λ_max (MeOH) nm ([θ]: 333 (+121702), 305 (−72578), 283 (−7335), 265 (−37555), 240 (+13386), 224 (−22870); FAB-MS (positive) m/z: 946 ([M+H]⁺), 581, 580, 549, 505, 366; HR-FAB-MS (positive) m/z: 946.2764 [M+H]+ (calcd for 946.2770, C₄₇H₄₈NO₂₀);

1H-NMR (DMSO-d₆) see Table S6; 13C-NMR (DMSO-d₆) see Table S8.

REFERENCES


