

Studies on the Constituents of *Swertia japonica* MAKINO II.¹⁾ On the Structures of New Glycosides

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Two new secoiridoid glycosides, swertiajaposide A (**1**) and swertiajaposide B (**2**), a new unsaturated alcohol glycoside, 3-butenyl 6'-*O*- α -L-arabinopyranosyl- β -D-glucopyranoside (**3**), and a new lignan glycoside, 7*R*,7'*R*,8*S*,8'*S*-(+)-neo-olivil-4-*O*- β -D-glucopyranoside (**4**), were isolated together with six known compounds from the whole plants of *Swertia japonica* MAKINO. The structures of the new compounds were elucidated on the basis of chemical and spectroscopic evidence.

Key words *Swertia japonica*; Gentianaceae; secoiridoid glycoside; unsaturated alcohol glycoside; lignan glycoside

The Japanese crude drug *Swertia* Herb (*Swertia japonica* MAKINO, Gentianaceae) has been used as a stomachic or stimulant of appetite. In a previous paper, we reported the isolation and structural elucidation of eight new secoiridoid diglycosides from the whole plants of *S. japonica*.¹⁾ Here, we report the isolation and structural elucidation of two new secoiridoid glycosides, swertiajaposide A (**1**) and swertiajaposide B (**2**), a new unsaturated alcohol glycoside, 3-butenyl 6'-*O*- α -L-arabinopyranosyl- β -D-glucopyranoside (**3**), and a new lignan glycoside, 7*R*,7'*R*,8*S*,8'*S*-(+)-neo-olivil-4-*O*- β -D-glucopyranoside (**4**), as well as six known compounds, 1-*O*- β -D-glucopyranosylamplexine (**5**),²⁾ boonein (**6**),³⁾ 5-hydroxymethylisochroman-1-one (**7**),⁴⁾ 3-hydroxybenzyl β -D-glucopyranoside (**8**),⁵⁾ 8-*O*-primeverosylbellidifolin (**9**)⁶⁾ and 2-*O*-[α -L-rhamnopyranosyl-(1 \rightarrow 2)- β -D-xylopyranosyl]-1,8-dihydroxy-6-methoxyxanthone (**10**).⁷⁾ Extraction and isolation were carried out as described in the Experimental section.

Compound **1**, $[\alpha]_D^{20} -121^\circ$ (MeOH), was isolated as an amorphous powder. The molecular formula was determined to be C₁₇H₂₄O₁₀ by high-resolution (HR)-FAB-MS. Acid hydrolysis of **1** gave D-glucose, which was identified by gas-liquid chromatography (GLC) analysis of their thiazolizidine derivatives.⁸⁾ The ¹H-NMR spectrum (*vide* Experimental) of **1**

showed signals due to a methylene [δ_H 2.47 (2H, m, H₂-6)], a methine [δ_H 3.07 (1H, br dd, *J*=8.8, 5.1 Hz, H-9)], a methoxyl group [δ_H 3.50 (3H, s)], an oxymethylene [δ_H 4.30 (1H, ddd, *J*=15.8, 11.0, 4.8 Hz, H-7A), 4.42 (1H, dd, *J*=11.0, 4.8 Hz, H-7B)], two acetal methines [δ_H 5.39 (1H, d, *J*=5.1 Hz, H-1), 5.47 (1H, s, H-3)] and a vinyl group [δ_H 5.34 (1H, ddd, *J*=16.9, 1.5, 0.7 Hz, H-10A), 5.35 (1H, dd, *J*=10.3, 1.5 Hz, H-10B), 5.73 (1H, ddd, *J*=16.9, 10.3, 8.8 Hz, H-8)]. Furthermore, an anomeric proton signal [δ_H 4.71 (1H, d, *J*=8.1 Hz, H-1')] was recognized. The coupling constant of an anomeric proton indicated that the glycosyl linkage is of β -configuration. The ¹³C-NMR spectrum (*vide* Experimental) showed signals due to a β -D-glucopyranosyl group [δ_C 62.8 (C-6'), 71.6 (C-4'), 74.7 (C-2'), 78.2 (C-3'), 78.5 (C-5'), 99.5 (C-1')] and a carbonyl group [δ_C 164.6 (C-11)]. By ¹H-¹H shift correlation spectroscopy (¹H-¹H COSY) and ¹H-detected heteronuclear multiple-bond connectivity (HMBC) spectra, the planar structure of **1** was deduced to be as shown in Fig. 1. The stereochemistry of **1** was determined from the difference rotating frame nuclear Overhauser effect (ROE) spectra (Fig. 2). An irradiation at δ 5.73 (H-8) produced ROE enhancement in the signal of the methoxyl group at C-3, whereas irradiation of the methoxyl

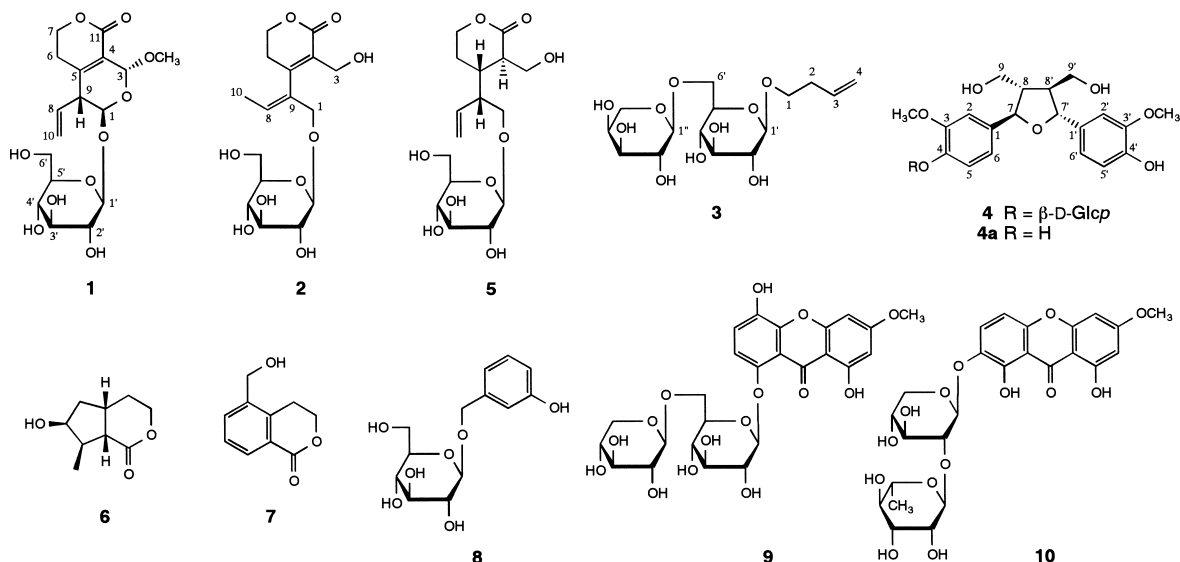
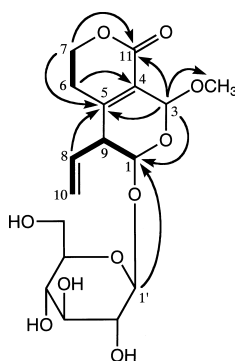
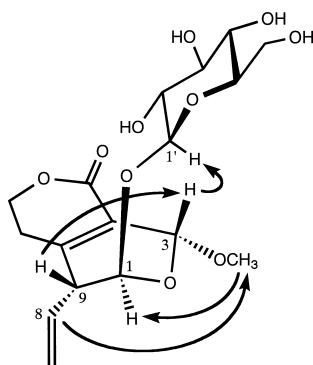


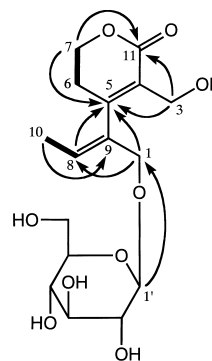
Chart 1

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Fig. 1. ^1H - ^1H COSY (Bold Lines) and HMBC (Arrows) Correlations for **1**Fig. 2. ROEs Detected for **1**

group at C-3 (δ 3.50) caused ROE enhancement in the signal of H-1 (δ 5.39), suggesting that H-1, a methoxyl group and a vinyl group occurred on the same face (α) of the molecule. On the other hand, irradiation at δ 3.07 (H-9) caused ROE enhancement in the signal of H-3 (δ 5.47) thereby establishing that these were on the same face (β). Furthermore, the ROE was observed between H-3 and H-1' (δ 4.71). From the above data, the structure of swertiajaposide A (**1**) was determined to be as shown in Chart 1. There is a possibility that compound **1** might be an artifact arising from the interaction of swertiamarin and methanol, because swertiamarin is the major secoiridoid glucoside of *S. japonica*, and methanol was used in the extraction and isolation procedures.⁹⁾

Compound **2**, $[\alpha]_{\text{D}} -25.6^\circ$ (MeOH), was isolated as an amorphous powder. The molecular formula was determined to be $\text{C}_{16}\text{H}_{24}\text{O}_9$ by HR-FAB-MS. Acid hydrolysis of **2** gave D-glucose, which was identified by GLC analysis of their thiazolizine derivatives.⁸⁾ The ^1H -NMR spectrum showed signals due to a methyl [δ_{H} 1.57 (3H, d, $J=6.8$ Hz, H₃-10)], a methylene [δ_{H} 2.61 (1H, m, H₂-6)], three oxymethylenes [δ_{H} 4.22 (1H, d, $J=12.0$ Hz, H-1A), 4.22 (2H, br s, H₂-3), 4.43 (2H, t, $J=6.8$ Hz, H₂-7), 4.49 (1H, d, $J=12.0$ Hz, H-1B)], an anomeric proton [δ_{H} 4.27 (1H, d, $J=7.8$ Hz, H-1')], and a trisubstituted double bond [δ_{H} 5.83 (1H, q, $J=6.8$ Hz, H-8)]. The ^{13}C -NMR spectrum showed signals due to a β -D-glucopyranosyl group [δ_{C} 62.9 (C-6'), 71.7 (C-4'), 75.1 (C-2'), 78.08 (C-3'), 78.14 (C-5'), 103.6 (C-1')], a fully substituted double bond [δ_{C} 129.2 (C-4), 155.1 (C-5)] and a carbonyl group [δ_{C} 167.2 (C-11)]. By ^1H - ^1H COSY and HMBC spectra, the planar structure of **2** was deduced to be as shown in Fig. 3. The geometry of the Δ^8 -double bond was shown to be *E* by the nuclear Overhauser effect correlation spectroscopy

Fig. 3. ^1H - ^1H COSY (Bold Lines) and HMBC (Arrows) Correlations for **2**

(NOESY) spectrum, giving a cross peak between H₂-1 and H-8. Thus, the structure of swertiajaposide B (**2**) was determined to be as shown in Chart 1.

Compound **3**, $[\alpha]_{\text{D}} -31.5^\circ$ (MeOH), was isolated as an amorphous powder. The molecular formula was determined to be $\text{C}_{15}\text{H}_{26}\text{O}_{10}$ by HR-FAB-MS. Acid hydrolysis gave L-arabinose and D-glucose, which were identified by GLC analysis of their thiazolizine derivatives.⁸⁾ The ^1H -NMR spectrum of **3** showed signals due to a methylene [δ_{H} 2.37 (1H, ddt, $J=6.8, 6.8, 1.2$ Hz, H-2A), 2.38 (1H, ddt, $J=7.1, 6.8, 1.5$ Hz, H-2B)], an oxymethylene [δ_{H} 3.90 (1H, dd, $J=9.5, 6.8$ Hz, H-1A), 3.92 (1H, dd, $J=9.5, 7.1$ Hz, H-1B)] and a vinyl group [δ_{H} 5.01 (1H, ddt, $J=10.2, 2.0, 1.2$ Hz, H-4A), 5.10 (1H, ddt, $J=17.3, 2.0, 1.5$ Hz, H-4B), 5.87 (1H, ddt, $J=17.3, 10.2, 6.8$ Hz, H-3)]. Further, the ^1H - and ^{13}C -NMR spectra indicated the presence of an α -L-arabinopyranosyl group [δ_{H} 4.31 (1H, d, $J=6.8$ Hz, H-1''); δ_{C} 66.7 (C-5''), 69.45 (C-4''), 72.4 (C-2''), 74.2 (C-3''), 105.1 (C-1'')], and a β -D-glucopyranosyl group [δ_{H} 4.27 (1H, d, $J=7.8$ Hz, H-1'); δ_{C} 69.48 (C-6'), 71.6 (C-4'), 75.0 (C-2'), 76.9 (C-5'), 78.0 (C-5'), 104.4 (C-1')]. The ^1H - ^1H COSY spectrum of **3** implied connectivities for H₂-1-H₂-2, H₂-2-H-3, and H-3-H₂-4. Interpretation of the HMBC spectrum revealed correlations from H-1' to C-1, and from H-1'' to C-6'. Based on this evidence, the structure of **3** was determined to be 3-butenyl 6'-O- α -L-arabinopyranosyl- β -D-glucopyranoside. Although 3-buten-1-ol has previously been isolated from the essential oil of coliza (rape),¹¹⁾ the diglycoside of this alcohol is the first naturally occurring.

Compound **4**, $[\alpha]_{\text{D}} +6.4^\circ$ (MeOH), was isolated as an amorphous powder. The molecular formula was determined to be $\text{C}_{26}\text{H}_{34}\text{O}_{12}$ by HR-FAB-MS. The ^1H -NMR spectrum showed signals due to two methines [δ_{H} 2.31 (2H, m, H-8, H-8')], two oxymethylenes [δ_{H} 3.57-3.73 (4H, m, H₂-9, H₂-9')], two methoxyl groups [δ_{H} 3.88 (3H, s, 3'-OCH₃), 3.89 (3H, s, 3-OCH₃)], an anomeric proton [δ_{H} 4.89 (1H, d, $J=7.6$ Hz, H-1'')], two oxymethines [δ_{H} 4.94 (1H, d, $J=8.4$ Hz, H-7), 4.98 (1H, d, $J=8.1$ Hz, H-7')], and two sets of 1,3,4-trisubstituted benzene protons [δ_{H} 6.78 (1H, d, $J=8.1$ Hz, H-5), 6.87 (1H, dd, $J=8.1, 1.7$ Hz, H-6'), 6.98 (1H, dd, $J=8.3, 2.0$ Hz, H-6), 7.03 (1H, d, $J=1.7$ Hz, H-2'), 7.11 (1H, d, $J=2.0$ Hz, H-2), 7.16 (1H, d, $J=8.3$ Hz, H-5)]. The ^{13}C -NMR spectrum showed signals due to a β -D-glucopyranosyl group [δ_{C} 62.6 (C-6''), 71.4 (C-4''), 74.5 (C-2''), 77.9 (C-3''), 78.3 (C-5''), 103.0 (C-1'')]. On enzymatic hydrolysis with β -glucosidase, **4** gave D-glucose and an aglycone

(4a). 4a was identified as a neo-olivil of all *trans* configuration types by the comparison of its ¹H-NMR spectrum and electron ionization (EI)-MS.¹² The optical rotation value of 4a ($[\alpha]_D^{25} +44^\circ$) is in agreement with that of 7*R*,7'*R*,8*S*,8'*S*-(+)-neo-olivil ($[\alpha]_D^{25} +49^\circ$).¹² The NOESY spectrum determined the position of the β-D-glucopyranosyl group to be at C-4, by showing correlations between H-1" and H-5. The circular dichroism (CD) spectrum of 4 showed a positive Cotton effect.^{13,14} On the basis of this evidence, the structure of 4 was determined to be 7*R*,7'*R*,8*S*,8'*S*-(+)-neo-olivil-4-*O*-β-D-glucopyranoside.

Experimental

General Procedures Optical rotations were determined using a JASCO DIP-360 digital polarimeter. UV spectra were recorded with a Beckman DU-64 spectrophotometer. CD spectrum was recorded with a JASCO J-720 spectropolarimeter. ¹H- and ¹³C-NMR spectra were recorded using JEOL JNM-LA 600 (600, 150 MHz, respectively) and JEOL JNM-LA 400 (400, 100 MHz, respectively) spectrometers. Chemical shifts are given on a δ (ppm) scale, with tetramethylsilane as an internal standard. The HR-EI-MS and HR-FAB-MS were recorded on a JEOL JMS-DX 303 mass spectrometer. Column chromatography was carried out on Kieselgel 60 (Merck; 230–400 mesh). Prep. HPLC was carried out on a Tosoh HPLC system (pump, CCPM; detector, UV-8020 or RI-8020); Condition A, Column, Cosmosil 5C18AR, 10 mm i.d.×25 cm (Nacalai Tesque); mobile phase, MeOH–H₂O (1:8); flow rate, 1.0 ml/min; RI detector; Condition B, Column, Cosmosil 5SL, 10 mm i.d.×25 cm (Nacalai Tesque); mobile phase, CH₂Cl₂–MeOH–H₂O (30:10:1); flow rate, 1.0 ml/min; UV detector, 225 nm. Condition C, Column, TSKgel ODS-120T, 7.8 mm i.d.×30 cm (Tosoh); mobile phase, MeOH; flow rate, 1.0 ml/min; UV detector, 225 nm. GLC was carried out on a Shimadzu GC-7A gas chromatograph.

Plant Material The dried whole plants of *S. japonica* were purchased from Uchida Wakanyaku Co. Ltd., Tokyo, Japan, in 2002.

Extraction and Isolation The dried whole plants of *S. japonica* (2.0 kg) were extracted with MeOH at room temperature. The MeOH extract was concentrated under reduced pressure. The MeOH extract (474 g) was suspended in water and this suspension was extracted with CHCl₃, Et₂O, AcOEt, *n*-BuOH and H₂O. The CHCl₃-soluble fraction was concentrated under reduced pressure to produce a residue (308.0 g). A part of this residue (17.8 g) was chromatographed on a silica-gel column using CHCl₃–MeOH (19:1), and the eluate was separated into 105 fractions (frs. 1–105). Fraction 60 was purified by prep. HPLC (Condition B) to give 6 (0.6 mg) and 7 (1.0 mg). The aqueous layer was passed through a Mitsubishi Diaion HP-20 column, and the adsorbed material was eluted with H₂O and MeOH. The MeOH eluate-fraction from the Diaion HP-20 column was concentrated. The residue (20.8 g) was chromatographed on a silica-gel column using CHCl₃–MeOH–H₂O (30:10:1), and the eluate was separated into 12 fractions (frs. 1–12). Fraction 6 was purified by prep. HPLC (Condition B) to give 4 (2.2 mg) and 8 (4.2 mg). Fraction 8 was purified by preparative HPLC (Condition B) to give 1 (6.1 mg), 2 (1.2 mg), 5 (8.0 mg), 9 (0.1 mg) and 10 (2.3 mg). Fraction 10 was purified by prep. HPLC (Condition A) to give 3 (7.3 mg).

All known compounds (5–10) were identified by comparison of their physical data with reported values.

Swertiajaposide A (1): Amorphous powder. $[\alpha]_D^{25} -121^\circ$ ($c=0.061$, MeOH). UV λ_{\max} (MeOH) nm (log ϵ): 205 (3.9), 220sh (3.8). HR-FAB-MS m/z : 411.1215 ($[\text{M}+\text{Na}]^+$, Calcd for C₁₇H₂₄O₁₀Na; 411.1267). ¹H-NMR (600 MHz, CD₃OD) δ : 2.47 (2H, m, H₂-6), 3.07 (1H, br dd, $J=8.8$, 5.1 Hz, H-9), 3.18 (1H, dd, $J=9.2$, 8.1 Hz, H-2'), 3.50 (3H, s, OCH₃), 3.66 (1H, dd, $J=12.1$, 5.5 Hz, H-6'A), 3.87 (1H, dd, $J=12.1$, 1.5 Hz, H-6'B), 4.30 (1H, ddd, $J=15.8$, 11.0, 4.8 Hz, H-7A), 4.42 (1H, dd, $J=11.0$, 4.8 Hz, H-7B), 4.71 (1H, d, $J=8.1$ Hz, H-1'), 5.34 (1H, ddd, $J=16.9$, 1.5, 0.7 Hz, H-10A), 5.35 (1H, dd, $J=10.3$, 1.5 Hz, H-10B), 5.39 (1H, d, $J=5.1$ Hz, H-1), 5.47 (1H, s, H-3), 5.73 (1H, ddd, $J=16.9$, 10.3, 8.8 Hz, H-8). ¹³C-NMR (150 MHz, CD₃OD) δ : 27.3 (C-6), 49.7 (C-9), 56.4 (OCH₃), 62.8 (C-6'), 67.2 (C-7), 71.6 (C-4'), 74.7 (C-2'), 78.2 (C-3'), 78.5 (C-5'), 94.9 (C-1), 95.9 (C-3), 99.5 (C-1'), 121.8 (C-10), 124.1 (C-4), 134.5 (C-8), 155.9 (C-5), 164.6 (C-11).

Swertiajaposide B (2): Amorphous powder. $[\alpha]_D^{25} -25.6^\circ$ ($c=0.117$, MeOH). UV λ_{\max} (MeOH) nm (log ϵ): 207 (3.9), 220sh (3.8), 250sh (1.9). HR-FAB-MS m/z : 383.1338 ($[\text{M}+\text{Na}]^+$, Calcd for C₁₆H₂₄O₉Na; 383.1318).

¹H-NMR (400 MHz, CD₃OD) δ : 1.57 (3H, d, $J=6.8$ Hz, H₃-10), 2.61 (2H, m, H₂-6), 3.15 (1H, dd, $J=9.0$, 7.8 Hz, H-2'), 3.64 (1H, dd, $J=12.0$, 5.4 Hz, H-6'A), 3.87 (1H, dd, $J=12.0$, 1.7 Hz, H-6'B), 4.22 (1H, d, $J=12.0$ Hz, H-1A), 4.22 (2H, br s, H₂-3), 4.27 (1H, d, $J=7.8$ Hz, H-1'), 4.43 (2H, t, $J=6.8$ Hz, H₂-7), 4.49 (1H, d, $J=12.0$ Hz, H-1B), 5.83 (1H, q, $J=6.8$ Hz, H-8). ¹³C-NMR (100 MHz, CD₃OD) δ : 14.8 (C-10), 29.5 (C-6), 58.0 (C-3), 62.9 (C-6'), 67.2 (C-7), 71.7 (C-4'), 72.9 (C-1), 75.1 (C-2'), 78.08 (C-3'), 78.14 (C-5'), 103.6 (C-1'), 128.4 (C-8), 129.2 (C-4), 136.5 (C-9), 155.1 (C-5), 167.2 (C-11).

3-Butenyl 6'-*O*- α -L-Arabinopyranosyl- β -D-glucopyranoside (3): Amorphous powder. $[\alpha]_D^{27} -31.5^\circ$ ($c=0.677$, MeOH). HR-FAB-MS m/z : 389.1404 ($[\text{M}+\text{Na}]^+$, Calcd for C₁₅H₂₆O₁₀Na; 389.1424). ¹H-NMR (400 MHz, CD₃OD) δ : 2.37 (1H, ddt, $J=6.8$, 6.8, 1.2 Hz, H-2A), 2.38 (1H, ddt, $J=7.1$, 6.8, 1.5 Hz, H-2B), 3.17 (1H, dd, $J=9.3$, 7.8 Hz, H-2'), 3.30–3.37 (2H, m, H-3', H-4'), 3.44 (1H, ddd, $J=9.8$, 5.6, 2.2 Hz, H-5'), 3.52 (1H, dd, $J=8.8$, 3.4 Hz, H-3''), 3.53 (1H, dd, $J=12.4$, 1.7 Hz, H-5'A), 3.59 (1H, dd, $J=8.8$, 6.8 Hz, H-2''), 3.72 (1H, dd, $J=11.5$, 5.6 Hz, H-6'A), 3.80 (1H, ddd, $J=3.4$, 3.4, 1.7 Hz, H-4''), 3.86 (1H, dd, $J=12.4$, 3.4 Hz, H-5'B), 3.90 (1H, dd, $J=9.5$, 6.8 Hz, H-1A), 3.92 (1H, dd, $J=9.5$, 7.1 Hz, H-1B), 4.09 (1H, dd, $J=11.5$, 2.2 Hz, H-6'B), 4.27 (1H, d, $J=7.8$ Hz, H-1'), 4.31 (1H, d, $J=6.8$ Hz, H-1''), 5.01 (1H, ddt, $J=10.2$, 2.0, 1.2 Hz, H-4A), 5.10 (1H, ddt, $J=17.3$, 2.0, 1.5 Hz, H-4B), 5.87 (1H, ddt, $J=17.3$, 10.2, 6.8 Hz, H-3). ¹³C-NMR (100 MHz, CD₃OD) δ : 35.3 (C-2), 66.7 (C-5''), 69.45 (C-4''), 69.48 (C-6'), 70.3 (C-1), 71.6 (C-4'), 72.4 (C-2''), 74.2 (C-3''), 75.0 (C-2'), 76.9 (C-5'), 78.0 (C-3'), 104.4 (C-1'), 105.1 (C-1''), 116.8 (C-4), 136.4 (C-3).

7*R*,7'*R*,8*S*,8'*S*-(+)-Neo-olivil 4-*O*-β-D-Glucopyranoside (4): Amorphous powder. $[\alpha]_D^{24} +6.4^\circ$ ($c=0.110$, MeOH). UV λ_{\max} (MeOH) nm (log ϵ): 228 (4.2), 277 (3.7). CD ($c=6.77 \times 10^{-5}$ M, MeOH) $\Delta\epsilon$ (nm): +11.8 (211), +6.7 (236), -0.3 (267), +0.3 (284). HR-FAB-MS m/z : 561.1902 ($[\text{M}+\text{Na}]^+$, Calcd for C₂₆H₃₄O₁₂Na; 561.1948). ¹H-NMR (600 MHz, CD₃OD, 40 °C) δ : 2.31 (2H, m, H-8, H-8'), 3.57–3.73 (4H, m, H₂-9, H₂-9'), 3.88 (3H, s, 3'-OCH₃), 3.89 (3H, s, 3-OCH₃), 4.89 (1H, d, $J=7.6$ Hz, H-1'), 4.94 (1H, d, $J=8.4$ Hz, H-7), 4.98 (1H, d, $J=8.1$ Hz, H-7'), 6.78 (1H, d, $J=8.1$ Hz, H-5'), 6.87 (1H, dd, $J=8.1$, 1.7 Hz, H-6'), 6.98 (1H, dd, $J=8.3$, 2.0 Hz, H-6), 7.03 (1H, d, $J=1.7$ Hz, H-2'), 7.11 (1H, d, $J=2.0$ Hz, H-2), 7.16 (1H, d, $J=8.3$ Hz, H-5). ¹³C-NMR (150 MHz, CD₃OD) δ : 55.3 (C-8), 55.5 (C-8'), 56.5 (OCH₃), 56.8 (OCH₃), 61.8 (C-9'), 61.9 (C-9), 62.6 (C-6''), 71.4 (C-4''), 74.5 (C-2''), 77.9 (C-3''), 78.3 (C-5''), 84.1 (C-7), 84.6 (C-7'), 103.0 (C-1''), 111.3 (C-2'), 111.9 (C-2), 116.1 (C-5'), 118.0 (C-5), 120.3 (C-6'), 120.6 (C-6), 134.9 (C-1'), 138.8 (C-1), 147.5 (C-4'), 147.6 (C-4), 149.2 (C-3'), 151.0 (C-3).

Determination of Absolute Structures of Sugar Moieties in 1–3

Each of compounds 1–3 (*ca.* 0.3 mg) was refluxed with 5% HCl for 2 h. The reaction mixture was neutralized with Ag₂CO₃ and filtered. The solution was concentrated *in vacuo* and dried to give a glycosyl residue which was subjected to preparation of the corresponding thiazolidine derivative, followed by trimethylsilylation and GLC analysis, according to the reported procedure. GLC conditions: column, G-column 1.2 mm i.d.×40 m; column temp., 245 °C; carrier gas, N₂ (32 ml/min); detector, FID. L-Arabinose t_R 22.4 min, D-glucose t_R 41.8 min (ref.: L-arabinose t_R 22.4 min, D-arabinose t_R 24.2 min, D-glucose t_R 41.8 min, L-glucose t_R 44.0 min).

Enzymatic Hydrolysis of 4 Compound 4 (1.6 mg) was treated with β-glucosidase (from sweet almonds, 1270 units/mg, Nacalai Tesque, 1.0 mg) in an AcOH–AcONa buffer solution (0.02 mol/l, pH 4.6, 1.5 ml). The mixture was stirred at 27 °C for 1 d, then extracted with an equal amount of AcOEt (×5), and the AcOEt layer was evaporated under reduced pressure. The residue was purified by prep. HPLC (Condition C) to give the aglycone (4a, 0.93 mg). The sugar, obtained by concentration of the water layer, was identified by GLC analysis to be D-glucose as its TMSi derivative. GLC conditions: column, 3%SE-52 on Chromosorb W (AW) (60–80 mesh, 3 mm i.d.×1.5 m); column temp., 160 °C; carrier gas, N₂ (40 ml/min); detector, FID. D-Glucose t_R 12.9 min and 20.5 min.

7*R*,7'*R*,8*S*,8'*S*-(+)-Neo-olivil (4a): Amorphous powder. $[\alpha]_D^{24} +44^\circ$ ($c=0.093$, EtOH). HR-EI-MS m/z : 376.1514 (M⁺, Calcd for C₂₀H₂₄O₇; 376.1522). ¹H-NMR (600 MHz, CD₃OD) δ : 2.32 (2H, m, H-8, H-8'), 3.60 (2H, dd, $J=11.4$, 5.5 Hz, H-9A, H-9'A), 3.69 (2H, dd, $J=11.4$, 3.7 Hz, H-9B, H-9'B), 3.88 (6H, s, OCH₃), 4.92 (2H, d, $J=8.7$ Hz, H-7, H-7'), 6.78 (2H, d, $J=8.1$ Hz, H-5, H-5'), 6.87 (2H, dd, $J=8.1$, 2.2 Hz, H-6, H-6'), 7.03 (2H, d, $J=2.2$ Hz, H-2, H-2').

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References and Notes

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