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→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**, $[\alpha]_D$ −121° (MeOH), was isolated as an amorphous powder. The molecular formula was determined to be $C_{17}H_{24}O_{10}$ by high-resolution (HR)-FAB-MS. Acid hydrolysis of **1** gave D-glucose, which was identified by gas-liquid chromatography (GLC) analysis of their thiazolizine derivatives.[8] The ^{1}H-NMR spectrum (*vide* Experimental) of **1** showed signals due to a methylene [δ_H 2.47 (2H, m, H_2-6)], 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 ^{13}C-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 ^{1}H–^{1}H shift correlation spectroscopy (^{1}H–^{1}H COSY) and ^{1}H-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

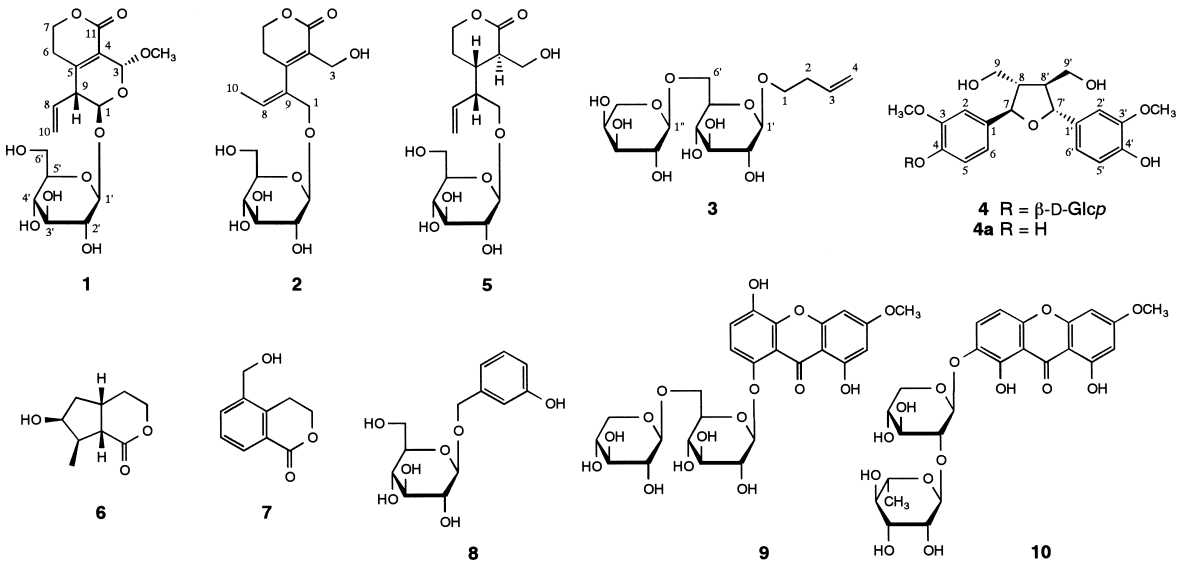

Chart 1

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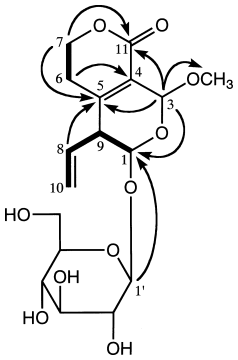

Fig. 1. ^{1}H–^{1}H COSY (Bold Lines) and HMBC (Arrows) Correlations for **1**

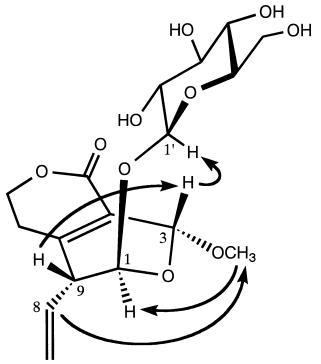

Fig. 2. ROEs Detected for **1**

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**, $[\alpha]_D$ −25.6° (MeOH), was isolated as an amorphous powder. The molecular formula was determined to be $C_{16}H_{24}O_9$ by HR-FAB-MS. Acid hydrolysis of **2** gave D-glucose, which was identified by GLC analysis of their thiazolizine derivatives.[8] The ^{1}H-NMR spectrum showed signals due to a methyl [δ_H 1.57 (3H, d, J=6.8 Hz, H_3-10)], a methylene [δ_H 2.61 (1H, m, H_2-6)], three oxymethylenes [δ_H 4.22 (1H, d, J=12.0 Hz, H-1A), 4.22 (2H, br s, H_2-3), 4.43 (2H, t, J=6.8 Hz, H_2-7), 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 ^{1}H–^{1}H 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

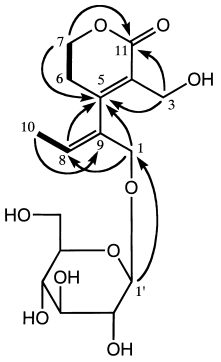

Fig. 3. ^{1}H–^{1}H COSY (Bold Lines) and HMBC (Arrows) Correlations for **2**

(NOESY) spectrum, giving a cross peak between H_2-1 and H-8. Thus, the structure of swertiajaposide B (**2**) was determined to be as shown in Chart 1.

Compound **3**, $[\alpha]_D$ −31.5° (MeOH), was isolated as an amorphous powder. The molecular formula was determined to be $C_{15}H_{26}O_{10}$ by HR-FAB-MS. Acid hydrolysis gave L-arabinose and D-glucose, which were identified by GLC analysis of their thiazolizine derivatives.[8] The ^{1}H-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 ^{1}H- 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″)][10] 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 ^{1}H–^{1}H COSY spectrum of **3** implied connectivities for H_2-1–H_2-2, H_2-2–H-3, and H-3–H_2-4. 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 occuring.

Compound **4**, $[\alpha]_D$ +6.4° (MeOH), was isolated as an amorphous powder. The molecular formula was determined to be $C_{26}H_{34}O_{12}$ by HR-FAB-MS. The ^{1}H-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, H_2-9, H_2-9′)], two methoxyl groups [δ_H 3.88 (3H, s, 3′-OCH_3), 3.89 (3H, s, 3-OCH_3)], 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 ^{1}H-NMR spectrum and electron ionization (EI)-MS.[12] The optical rotation value of **4a** ($[\alpha]_D$ +44°) is in agreement with that of 7*R*,7′*R*,8*S*,8′*S*-(+)-neo-olivil ($[\alpha]_D$ +49°).[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. ^{1}H- and ^{13}C-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–H_2O (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, CH_2Cl_2–MeOH–H_2O (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 $CHCl_3$, Et_2O, AcOEt, *n*-BuOH and H_2O. The $CHCl_3$-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 $CHCl_3$–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 H_2O 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 $CHCl_3$–MeOH–H_2O (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° (*c*=0.061, MeOH). UV λ_{max} (MeOH) nm (log ε): 205 (3.9), 220sh (3.8). HR-FAB-MS *m/z*: 411.1215 ($[M+Na]^+$, Calcd for $C_{17}H_{24}O_{10}Na$; 411.1267). ^{1}H-NMR (600 MHz, CD_3OD) δ: 2.47 (2H, m, H_2-6), 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, OCH_3), 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). ^{13}C-NMR (150 MHz, CD_3OD) δ: 27.3 (C-6), 49.7 (C-9), 56.4 (OCH_3), 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° (*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 ($[M+Na]^+$, Calcd for $C_{16}H_{24}O_9Na$; 383.1318). ^{1}H-NMR (400 MHz, CD_3OD) δ: 1.57 (3H, d, *J*=6.8 Hz, H_3-10), 2.61 (2H, m, H_2-6), 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, H_2-3), 4.27 (1H, d, *J*=7.8 Hz, H-1′), 4.43 (2H, t, *J*=6.8 Hz, H_2-7), 4.49 (1H, d, *J*=12.0 Hz, H-1B), 5.83 (1H, q, *J*=6.8 Hz, H-8). ^{13}C-NMR (100 MHz, CD_3OD) 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° (*c*=0.677, MeOH). HR-FAB-MS *m/z*: 389.1404 ($[M+Na]^+$, Calcd for $C_{15}H_{26}O_{10}Na$; 389.1424). ^{1}H-NMR (400 MHz, CD_3OD) 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). ^{13}C-NMR (100 MHz, CD_3OD) 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° (*c*=0.110, MeOH). UV λ_{max} (MeOH) nm (log ε): 228 (4.2), 277 (3.7). CD (*c*=6.77×10^{-5} M, MeOH) $\Delta\varepsilon$ (nm): +11.8 (211), +6.7 (236), −0.3 (267), +0.3 (284). HR-FAB-MS *m/z*: 561.1902 ($[M+Na]^+$, Calcd for $C_{26}H_{34}O_{12}Na$; 561.1948). ^{1}H-NMR (600 MHz, CD_3OD, 40 °C) δ: 2.31 (2H, m, H-8, H-8′), 3.57—3.73 (4H, m, H_2-9, H_2-9′), 3.88 (3H, s, 3′-OCH_3), 3.89 (3H, s, 3-OCH_3), 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). ^{13}C-NMR (150 MHz, CD_3OD) δ: 55.3 (C-8), 55.5 (C-8′), 56.5 (OCH_3), 56.8 (OCH_3), 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 Ag_2CO_3 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, N_2 (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, N_2 (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° (*c*=0.093, EtOH). HR-EI-MS *m/z*: 376.1514 (M^+, Calcd for $C_{20}H_{24}O_7$; 376.1522). ^{1}H-NMR (600 MHz, CD_3OD) 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, OCH_3), 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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