# Studies on the Constituents of *Syringa* Species. X.[1] Five New Iridoid Glycosides from the Leaves of *Syringa reticulata* (BLUME) HARA

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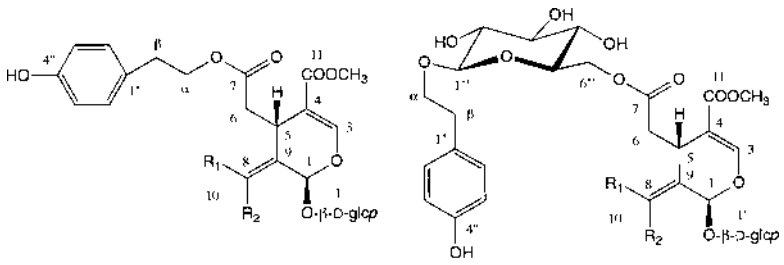
**Five new iridoid glycosides, (8*Z*)-ligstroside (1), (8*Z*)-nüzhenide (3), 6′-*O*-α-D-glucopyranosylsyringopicroside (4), 3′-*O*-β-D-glucopyranosylsyringopicroside (5) and 4′-*O*-β-D-glucopyranosylsyringopicroside (6) were isolated, together with a known one, (8*E*)-nüzhenide (2), from the leaves of *Syringa reticulata*. Their structures were established on the basis of chemical and spectral data. Compounds 1 and 3 are the first findings of a (8*Z*)-oleoside-type secoiridoid. Compound 4 is the first naturally occurring iridoid di-glycoside having an isomaltose.**

**Key words** *Syringa reticulata*; Oleaceae; (8*Z*)-ligstroside; (8*Z*)-nüzhenide; iridoid di-glycoside; isomaltose

In previous papers, we reported on the isolation of eleven new glycosides from the leaves of *Syringa reticulata* (BLUME) HARA.[2—5] In the course of further studies on the constituents of the above plant, five new iridoid glycosides (**1**, **3**—**6**) along with a known one (**2**) have been isolated. This paper deals with the structural elucidation and identification of these compounds. The isolation procedure is described in detail in the Experimental section. Compound **2** was identified as (8*E*)-nüzhenide by comparison of the spectral data with those reported in the literature.[6]

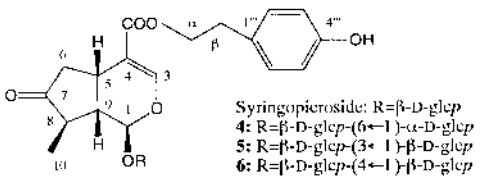
Compound **1** was obtained as an amorphous powder, $[\alpha]_D^{26}$ −81.3° (MeOH). The molecular formula of **1**, $C_{25}H_{32}O_{12}$, was confirmed by high-resolution (HR)-FAB-MS and was coincident with that of (8*E*)-ligstroside[7,8] isolated from the same plant.[5] Its $^1$H-NMR spectral pattern was very similar to that of (8*E*)-ligstroside, except for the chemical shifts owing to 1-H, 5-H, 6-$H_2$, 8-H, 10-$H_3$ and 1′-H, respectively.[9] The $^1$H–$^1$H shift correlation spectroscopy (COSY) and $^1$H-detected heteronuclear multiple bond correlation (HMBC, Fig. 1) experiments of **1** made up the same plane structure as (8*E*)-ligstroside, suggesting that **1** is the 8*Z*-isomer of (8*E*)-ligstroside. The stereochemistry of **1** was defined by the $^1$H–$^1$H COSY and nuclear Overhauser enhancement spectroscopy (NOESY) experiments. As shown in Fig. 2, the NOE correlations and homoallylic coupling of (8*E*)-ligstroside indicated that both 1-H and 6-$H_2$ were quasi-axial with respect to the dihydropyran ring. On the other hand, the NOE correlations (1-H/10-$H_3$, 5-H/8-H, 6-$H_2$/8-H), and homoallylic (5-H/10-$H_3$) and allylic (3-H/5-H) couplings of **1** indicated that the geometry of the olefinic bond at C-8 is the *Z*-configuration, and both 1-H and 6-$H_2$ are quasi-equatorial with respect to the dihydropyran ring. Consequently, the structure of **1** was determined to be (8*Z*)-ligstroside.

Compound **3** was obtained as an amorphous powder, $[\alpha]_D^{26}$ −101.1° (MeOH). The molecular formula of **3**, $C_{31}H_{42}O_{17}$, was confirmed by HR-FAB-MS and was coincident with that of **2**. Its $^1$H-NMR spectral pattern was similar to that of **2**, except for the chemical shifts owing to 1-H, 5-H, 6-$H_2$, 8-H, 10-$H_3$ and 1′-H, respectively. With regard to these proton signals of **3**, the chemical shifts were almost the same as those of **1**. The $^1$H–$^1$H COSY and HMBC (Fig. 1) experiments of **3** made up the same plane structure as **2**, suggesting that **3** is the 8*Z*-isomer of **2**. As shown in Fig. 2, the NOE correlations (1-H/10-$H_3$, 5-H/8-H, 6-$H_2$/8-H), and homoallylic (5-H/10-




(8*E*)-ligstroside: $R_1$=$CH_3$, $R_2$=H
**1** [(8*Z*)-ligstroside]: $R_1$=H, $R_2$=$CH_3$

**2** [(8*E*)-nüzhenide]: $R_1$=$CH_3$, $R_2$=H
**3** [(8*Z*)-nüzhenide]: $R_1$=H, $R_2$=$CH_3$




Syringopicroside: R=β-D-glc*p*
**4:** R=β-D-glc*p*-(6←1)-α-D-glc*p*
**5:** R=β-D-glc*p*-(3← 1)-β-D-glc*p*
**6:** R=β-D-glc*p*-(4←1)-β-D-glc*p*

Chart 1

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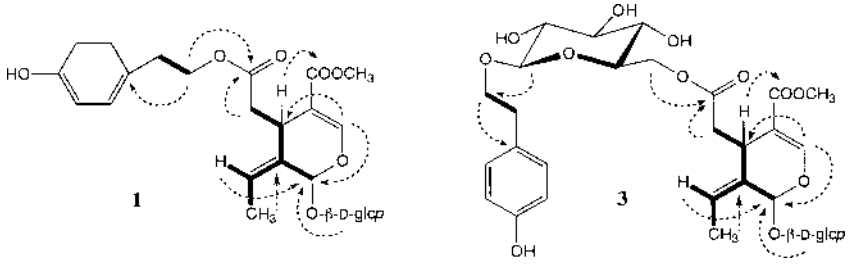


Fig. 1. The Main HMBC Correlation

Heavy lines indicate partial structures inferred from $^1$H–$^1$H COSY.

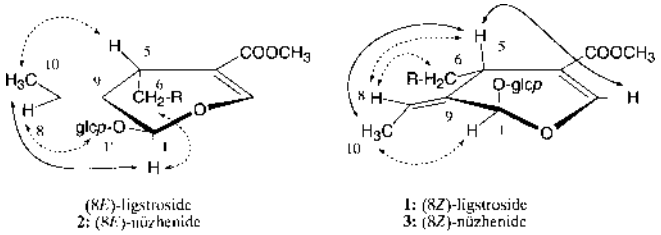


Fig. 2. NOE Correlations and Long-Range Couplings

◂⟶ NOE, ◂⟶ long-range coupling.

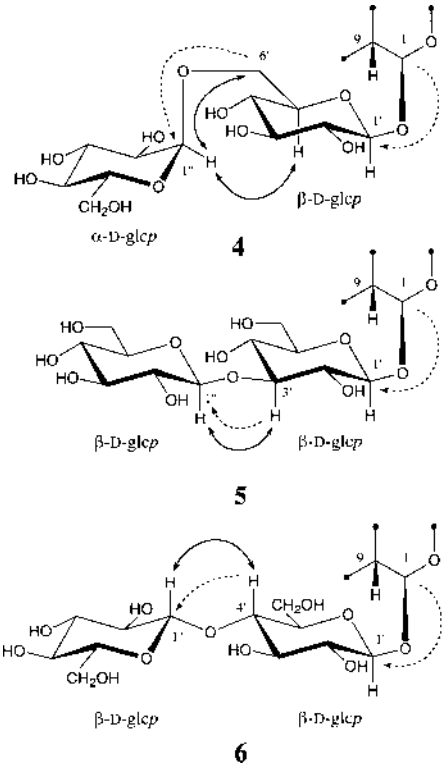


Fig. 3. Diagnostic HMBC and NOE Correlations for **4**, **5** and **6**

◂----- HMBC, ◂⟶ NOE.

$H_3$) and allylic (3-H/5-H) couplings of **3** indicated that the geometry of the olefinic bond at C-8 is the *Z*-configuration, and both 1-H and 6-$H_2$ are quasi-equatorial with respect to the dihydropyran ring. Consequently, the structure of **3** was determined to be (8*Z*)-nüzhenide. It is likely that the conformational changes of the dihyroropyran rings arise from steric hindrance between the $\beta$-D-glucopyranose attached C-1 and 10-$CH_3$.

Compound **4** was obtained as an amorphous powder, $[\alpha]_D^{26}$ −28.6° (MeOH). The molecular formula of **4**, $C_{30}H_{40}O_{16}$, was confirmed by HR-FAB-MS. The $^{13}$C-NMR spectrum of **4** was similar to that of syringopicroside[10] isolated from the same plant,[3,11] except for the presence of an additional hexosyl moiety and difference in the chemical shift at C-6′ position [$\delta$ 68.0 (+5.2 ppm)]. In the $^1$H-NMR spectrum of **4**, the coupling constant of the anomeric proton signal of the additional hexosyl moiety was 3.7 Hz ($\delta$ 4.83). Acid hydrolysis of **4** gave only D-glucose, which was identified by gas-liquid chromatography (GLC) after conversion to the TMSi ether of thiazolidine derivative.[12] These indicated that the additional $\alpha$-D-glucopyranosyl moiety in **4** is attached to 6′-OH in syringopicroside. This finding was supported by the NOE and HMBC correlations (Fig. 3). Consequently, the structure of **4** was determined to be 6′-*O*-$\alpha$-D-glucopyranosylsyringopicroside. Compound **4** is the first naturally occurring iridoid diglycoside having an isomaltose.

Compound **5** was obtained as an amorphous powder, $[\alpha]_D^{26}$ −88.9° (MeOH). The molecular formula of **5**, $C_{30}H_{40}O_{16}$, was confirmed by HR-FAB-MS and was coincident with that of **4**. The $^{13}$C-NMR spectrum of **5** was similar to that of syringopicroside, except for the presence of an additional hexosyl moiety and difference in the chemical shift at C-3′ position [$\delta$ 87.5 (+9.4 ppm)]. In the $^1$H-NMR spectrum of **5**, the coupling constant of the anomeric proton signal of the additional hexosyl moiety was 8.1 Hz ($\delta$ 4.57). Acid hydrolysis proved that both of two sugars in **5** are D-glucose in the above manner. These indicated that the additional $\beta$-D-glucopyranosyl moiety in **5** is attached to 3′-OH in syringopicroside. This finding was supported by the NOE and HMBC correlations (Fig. 3). Consequently, the structure of **5** was determined to be 3′-*O*-$\beta$-D-glucopyranosylsyringopicroside.

Compound **6** was obtained as an amorphous powder, $[\alpha]_D^{26}$ −77.2° (MeOH). The molecular formula of **6**, $C_{30}H_{40}O_{16}$, was confirmed by HR-FAB-MS and was coincident with that of **5**. The $^1$H-NMR spectrum of **6** resembled that of **5** except for the shift of the signal assigned to the additional anomeric proton [$\delta$ 4.40 (d, $J$=7.8 Hz)]. In the $^{13}$C-NMR spectrum, the C-4′ signal ($\delta$ 80.6) of **6** was shifted downfield by 9.0 ppm compared with that of syringopicroside. Acid hydrolysis proved that both of two sugars in **6** are D-glucose in the above manner. These indicated that the additional $\beta$-D-glucopyranosyl moiety in **6** is attached to 4′-OH in syringopicroside. This finding was supported by the NOE and HMBC correlations (Fig. 3). Consequently, the structure of **6** was determined to be 4′-*O*-$\beta$-D-glucopyranosylsyringopicroside.

The iridoid glycoside which comprises an oleoside moiety as a framework is called oleoside-type secoiridoid, and this

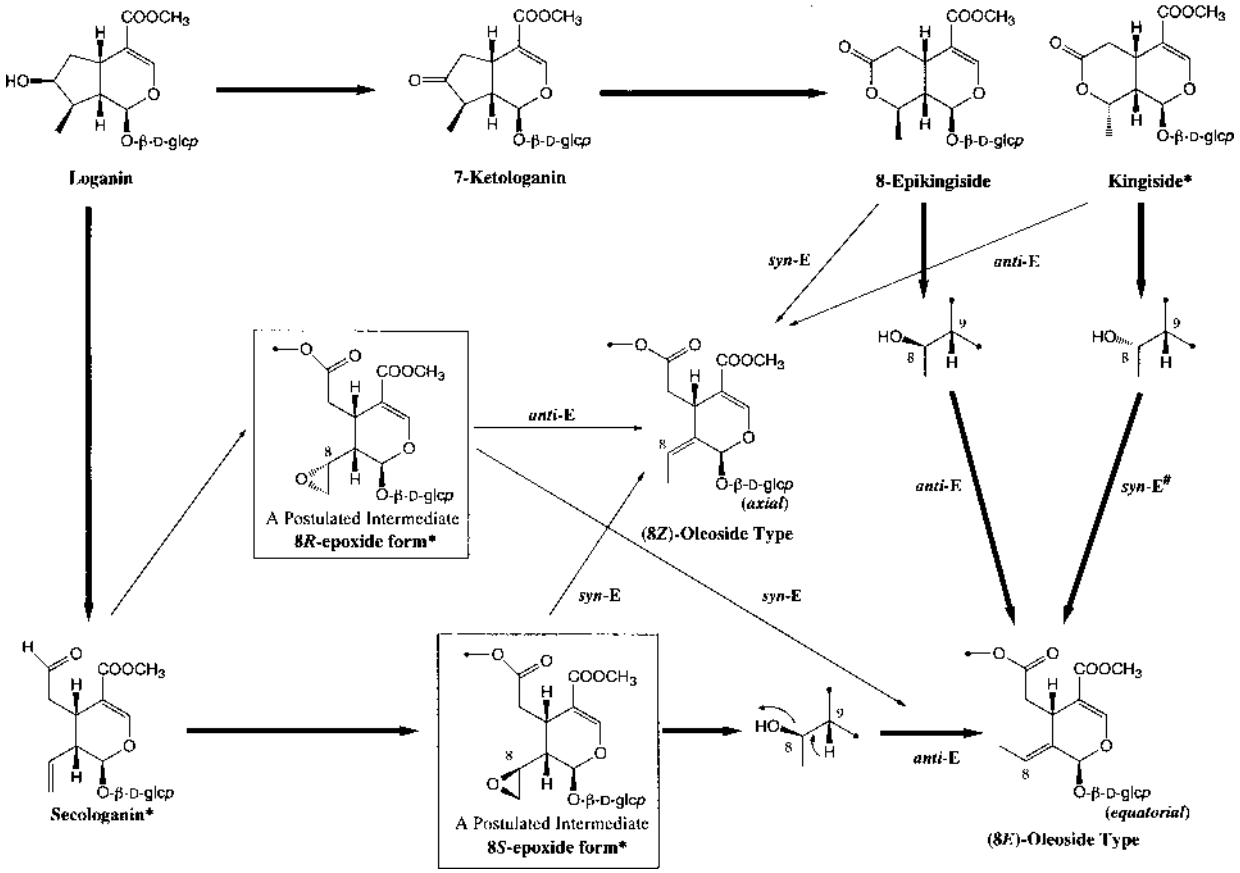


Fig. 4. Possible Biosynthetic Pathways of Oleoside-Type Secoiridoids

E=Elimination. * They are not yet identified from the leaves of *S. reticulata*. # It is not associated with the general concept of a stereoselective enzymatic reaction, but probably arises from the steric hindrance between glucopyranose attached C-1 and 10-$CH_3$.

type occurs only in Oleaceae plants. All of them isolated so far have *E*-configuration of the olefinic bond at C-8. Compounds **1** and **3** are the first findings of a (8*Z*)-oleoside-type secoiridoid. From a biosynthetic point of view, it is interesting to note that (8*Z*)-oleoside-type secoiridoid was isolated from a natural source. Previous biosynthetic investigations (bold lines) of (8*E*)-oleoside-type secoiridoid reported by Inouye *et al.*[13,14] and our structural studies described above presume that these type secoiridoids are biosynthesized by the route depicted in Fig. 4.

## Experimental

**General** Optical rotation were taken with a JASCO DIP-360 digital polarimeter. UV spectra were recorded with a Beckman DU-64 spectrometer. The $^1$H- and $^{13}$C-NMR spectra were recorded with JEOL JNM-GSX 400 (400 MHz, 100 MHz, respectively) and JEOL JNM-LA 600 (600 MHz, 150 MHz, respectively) spectrometers. Chemical shifts are given on a $\delta$ (ppm) scale with tetramethylsilane (TMS) as an internal standard. FAB-MS were recorded on a JEOL JMS-DX 303 mass spectrometer. Column chromatography was carried out on Kieselgel 60 (Merck; 70—230 mesh), Cosmosil 75$C_{18}$-OPN (Nacalai Tesque) and Sephadex LH-20 (Pharmacia Fine Chemicals). Preparative HPLC was carried out on a Tosoh HPLC system [pump, CCPS; detector, UV-8020; column, Cosmosil 5$C_{18}$-AR (10 mm i.d.×25 cm, Nacalai Tesque), Cosmosil 5SL (10 mm i.d.×25 cm, Nacalai Tesque)]. GLC was carried out on a Shimadzu GC-7A equipped with hydrogen flame ionization detector (FID).

**Material** The leaves of *S. reticulata* were collected near Sendai, Miyagi prefecture, Japan, in July 1985 and identified by one of the authors (M. Kikuchi). A voucher specimen is held in the laboratory of M. Kikuchi.

**Isolation** Fresh leaves of *S. reticulata* (3.8 kg) were extracted with MeOH at room temperature for 10 d. The MeOH extract was concentrated under reduced pressure and the residue was suspended in water. This suspension was successively 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 (88.2 g). The extract (25.0 g) was suspended in MeOH–$H_2O$ (3 : 1, 60 ml), and the soluble material (18.0 g) was chromatographed on a $C_{18}$ open column using MeOH–$H_2O$ (3 : 1) and the eluate was separated into seven fractions (frs. 1—7). Fraction 1 was rechromatographed on a silica gel column using $CHCl_3$–MeOH (9 : 1, 5 : 1, 1 : 1) and the eluate was separated into eleven fractions (frs. 1-1—1-11). Fraction 1—6 was subjected to preparative HPLC [column, Cosmosil 5$C_{18}$-AR; mobile phase, MeOH–$H_2O$ (1 : 1); UV detector, 224 nm: column, Cosmosil 5SL; mobile phase, $CHCl_3$–MeOH–$H_2O$ (30 : 10 : 1); UV detector, 230 nm; each flow rate: 1.5 ml/min] to give (8*E*)-ligstroside (370.5 mg), syringopicroside (25.0 mg) and compound **1** (10.0 mg). The *n*-BuOH-soluble fraction was concentrated under reduced pressure to produce a residue (107.0 g). The extract (25.0 g) was chromatographed on a silica gel column using $CHCl_3$–MeOH (10 : 3, 5 : 2, 2 : 1, 1 : 1, 2 : 3) and the eluate was separated into three fractions (frs. 1—3). Fraction 1 was rechromatographed on a silica gel column using $CHCl_3$–MeOH (5 : 1, 1 : 1) and the eluate was separated into seven fractions (frs. 1-1—1-7). Fraction 1—4 was chromatographed on a Sephadex LH-20 column using 50% MeOH and the eluate was separated into five fractions (frs. 1-4-1—1-4-5). Fraction 1-4-2 was subjected to preparative HPLC [column, Cosmosil 5$C_{18}$-AR; mobile phase, MeOH–$H_2O$ (2 : 3); UV detector, 225 nm: column, Cosmosil 5SL; mobile phase, $CHCl_3$–MeOH–$H_2O$ (30 : 10 : 1); UV detector, 230 nm; each flow rate; 1.5 ml/min] to give syringopicroside (30.0 mg), compounds **2** (32.5 mg), **3** (8.0 mg), **4** (7.5 mg), **5** (13.0 mg) and **6** (28.0 mg).

**(8*Z*)-Ligstroside (1)** An amorphous powder, $[\alpha]_D^{26}$ −81.3° (*c*=0.2, MeOH); UV $\lambda_{max}$ (MeOH) nm (log $\varepsilon$): 276 (3.41), 225 (4.25). FAB-MS *m/z*: 547 $[M+Na]^+$. HR-FAB-MS *m/z*: 547.1825 $[M+Na]^+$ ($C_{25}H_{32}O_{12}Na$, Calcd for 547.1791). $^1$H-NMR (400 MHz, $CD_3OD$) $\delta$: 7.45 (1H, d, *J*=1.2 Hz, 3-H), 7.04 (2H, d, *J*=8.5 Hz, 2″, 6″-H), 6.72 (2H, d, *J*=8.5 Hz, 3″, 5″-H), 6.23 (1H, br s, 1-H), 5.48 (1H, dq, *J*=7.1, 1.0 Hz, 8-H), 4.64 (1H, d, *J*=7.8 Hz, 1′-H), 4.19 (2H, m, $\alpha$-$H_2$), 3.91 (1H, dd, *J*=12.0, 2.0 Hz, 6′-$H_B$), 3.68 (3H, s, 11-$COOCH_3$), 3.66 (2H, m, 5-H, 6′-$H_A$), 3.27—3.38 (3H, m, 3′, 4′, 5′-H),

3.19 (1H, dd, $J$=8.8, 7.8 Hz, 2′-H), 2.89 (1H, dd, $J$=15.6, 3.8 Hz, 6-$H_B$), 2.81 (2H, t, $J$=6.8 Hz, $\beta$-$H_2$), 2.62 (1H, dd, $J$=15.6, 8.1 Hz, 6-$H_A$), 1.71 (3H, dd, $J$=7.1, 1.7 Hz, 10-$H_3$). $^{13}$C-NMR (100 MHz, $CD_3OD$): Table 1.

**(8*E*)-Nüzhenide (2)** An amorphous powder, $[\alpha]_D^{26}$ −140.0° ($c$=0.6, MeOH). FAB-MS $m/z$: 709 $[M+Na]^+$. $^1$H-NMR (400 MHz, $CD_3OD$) $\delta$: 7.51 (1H, s, 3-H), 7.05 (2H, d, $J$=8.5 Hz, 2″, 6″-H), 6.68 (2H, d, $J$=8.5 Hz, 3″, 5″-H), 6.09 (1H, br q, $J$=7.5 Hz, 8-H), 5.92 (1H, br s, 1-H), 4.80 (1H, d, $J$=7.8 Hz, 1′-H), 4.34 (1H, dd, $J$=12.0, 2.2 Hz, 6‴-$H_B$), 4.30 (1H, d, $J$=8.1 Hz, 1‴-H), 4.20 (1H, dd, $J$=12.0, 5.6 Hz, 6‴-$H_A$), 4.00 (1H, dd, $J$=8.8, 4.9 Hz, 5-H), 3.95 (1H, br t, $J$=7.5 Hz, $\alpha$-$H_B$), 3.88 (1H, dd, $J$=12.2, 1.5 Hz, 6′-$H_B$), 3.68 (3H, s, 11-$COOCH_3$), 3.68 (2H, m, $\alpha$-$H_A$, 6′-$H_A$), 3.29—3.47 (7H, m, 2′, 3′, 4′, 5′-H, 3‴, 4‴, 5‴-H), 3.19 (1H, dd, $J$=8.8, 8.1 Hz, 2‴-H), 2.83 (2H, br t, $J$=7.5 Hz, $\beta$-$H_2$), 2.75 (1H, dd, $J$=14.4, 4.9 Hz, 6-$H_B$), 2.49 (1H, dd, $J$=14.4, 8.8 Hz, 6-$H_A$), 1.72 (3H, dd, $J$=7.1, 1.5 Hz, 10-$H_3$). The spectral data were identified by those of reported data.[6)]

**(8*Z*)-Nüzhenide (3)** An amorphous powder, $[\alpha]_D^{26}$ −101.1° ($c$=1.0, MeOH); UV $\lambda_{max}$ (MeOH) nm (log $\varepsilon$): 276 (3.24), 225 (4.10). FAB-MS $m/z$: 709 $[M+Na]^+$. HR-FAB-MS $m/z$: 709.2343 $[M+Na]^+$ ($C_{31}H_{42}O_{17}Na$, Calcd for 709.2320). $^1$H-NMR (400 MHz, $CD_3OD$) $\delta$: 7.46 (1H, d, $J$=1.5 Hz, 3-H), 7.05 (2H, d, $J$=8.5 Hz, 2″, 6″-H), 6.69 (2H, d, $J$=8.5 Hz, 3″, 5″-H), 6.24 (1H, s, 1-H), 5.67 (1H, br q, $J$=7.1 Hz, 8-H), 4.67 (1H, d, $J$=7.8 Hz, 1′-H), 4.42 (1H, dd, $J$=12.0, 2.0 Hz, 6‴-$H_B$), 4.29 (1H, d, $J$=7.8 Hz, 1‴-H), 4.16 (1H, dd, $J$=12.0, 5.6 Hz, 6‴-$H_A$), 3.96 (1H, dt, $J$=9.5, 7.8 Hz, $\alpha$-$H_B$), 3.90 (1H, dd, $J$=12.0, 2.0 Hz, 6′-$H_B$), 3.70 (3H, m, 5-H, 6′-HA, $\alpha$-$H_A$), 3.66 (3H, s, 11-$COOCH_3$), 3.27—3.45 (6H, m, 3′, 4′, 5′-H, 3‴, 4‴, 5‴-H), 3.20 (2H, m, 2′, 2‴-H), 2.93 (1H, dd, $J$=15.7, 4.0 Hz, 6-$H_B$), 2.84 (2H, br t, $J$=7.8 Hz, $\beta$-$H_2$), 2.73 (1H, dd, $J$=15.7, 7.8 Hz, 6-$H_A$), 1.75 (3H, dd, $J$=7.1, 1.7 Hz, 10-$H_3$). $^{13}$C-NMR (100 MHz, $CD_3OD$): Table 1.

**6′-*O*-$\alpha$-D-Glucopyranosylsyringopicroside (4)** An amorphous powder, $[\alpha]_D^{26}$ −28.6° ($c$=0.2, MeOH); UV $\lambda_{max}$ (MeOH) nm (log $\varepsilon$): 276 (3.30), 225 (4.10). FAB-MS $m/z$: 679 $[M+Na]^+$. HR-FAB-MS $m/z$: 679.2196 $[M+Na]^+$ ($C_{30}H_{40}O_{16}Na$, Calcd for 679.2214). $^1$H-NMR (600 MHz, $CD_3OD$) $\delta$: 7.44 (1H, d, $J$=1.5 Hz, 3-H), 7.04 (2H, d, $J$=8.8 Hz, 2‴, 6‴-H), 6.71 (2H, d, $J$=8.8 Hz, 3‴, 5‴-H), 5.55 (1H, d, $J$=3.7 Hz, 1-H), 4.83 (1H, d, $J$=3.7 Hz, 1″-H), 4.70 (1H, d, $J$=8.1 Hz, 1′-H), 4.26, 4.25 (each 1H, t, $J$=7.0 Hz, $\alpha$-$H_2$), 3.90 (1H, dd, $J$=11.4, 5.5 Hz, 6′-$H_B$), 3.80 (1H, dd, $J$=11.4, 2.0 Hz, 6′-$H_A$), 3.79 (1H, dd, $J$=10.0, 2.0 Hz, 6″-$H_B$), 3.65 (1H, t, $J$=9.5 Hz, 3″-H), 3.64 (1H, dd, $J$=10.0, 5.5 Hz, 6″-$H_A$), 3.63 (1H, m, 5″-H), 3.53 (1H, ddd, $J$=9.5, 5.5, 2.0 Hz, 5′-H), 3.27—3.38 (4H, m, 3′, 4′-H, 2″, 4″-H), 3.29 (1H, dd, $J$=8.8, 8.1 Hz, 2′-H), 3.29 (1H, m, 5-H), 2.84 (2H, t, $J$=7.0 Hz, $\beta$-$H_2$), 2.56 (1H, dd, $J$=19.4, 8.4 Hz, 6-H$\beta$), 2.43 (1H, dd, $J$=19.4, 1.5 Hz, 6-H$\alpha$), 2.31 (1H, ddd, $J$=9.5, 7.3, 3.7 Hz, 9-H), 2.12 (1H, dq, $J$=9.5, 7.3 Hz, 8-H), 1.15 (3H, d, $J$=7.3 Hz, 10-$H_3$). $^{13}$C-NMR (150 MHz, $CD_3OD$): Table 2.

**3′-*O*-$\beta$-D-Glucopyranosylsyringopicroside (5)** An amorphous powder, $[\alpha]_D^{26}$ −88.9° ($c$=0.3, MeOH); UV $\lambda_{max}$ (MeOH) nm (log $\varepsilon$): 276 (3.38), 224 (4.11). FAB-MS $m/z$: 679 $[M+Na]^+$. HR-FAB-MS $m/z$: 679.2246 $[M+Na]^+$ ($C_{30}H_{40}O_{16}Na$, Calcd for 679.2214). $^1$H-NMR (600 MHz, $CD_3OD$) $\delta$: 7.43 (1H, d, $J$=1.5 Hz, 3-H), 7.04 (2H, d, $J$=8.4 Hz, 2‴, 6‴-H), 6.71 (2H, d, $J$=8.4 Hz, 3‴, 5‴-H), 5.61 (1H, d, $J$=3.3 Hz, 1-H), 4.72 (1H, d, $J$=8.1 Hz, 1′-H), 4.57 (1H, d, $J$=8.1 Hz, 1″-H), 4.26, 4.25 (each 1H, t, $J$=7.0 Hz, $\alpha$-$H_2$), 3.91 (1H, dd, $J$=11.7, 2.0 Hz, 6′-$H_B$), 3.88 (1H, dd, $J$=12.1, 2.2 Hz, 6″-$H_B$), 3.67 (1H, dd, $J$=11.7, 5.5 Hz, 6′-$H_A$), 3.63 (1H, dd, $J$=12.1, 6.2 Hz, 6″-$H_A$), 3.58 (1H, dd, $J$=8.8, 8.4 Hz, 3′-H), 3.21—3.41 (8H, m, 5-H, 2′, 4′, 5′-H, 2″, 3″, 4″, 5″-H), 2.84 (2H, t, $J$=7.0 Hz, $\beta$-$H_2$), 2.56 (1H, dd, $J$=19.1, 8.3 Hz, 6-H$\beta$), 2.43 (1H, br d, $J$=19.1 Hz, 6-H$\alpha$), 2.32 (1H, ddd, $J$=9.9, 7.7, 3.3 Hz, 9-H), 2.11 (1H, br q, $J$=7.0 Hz, 8-H), 1.14 (3H, d, $J$=7.0 Hz, 10-$H_3$). $^{13}$C-NMR (150 MHz, $CD_3OD$): Table 2.

**4′-*O*-$\beta$-D-Glucopyranosylsyringopicroside (6)** An amorphous powder, $[\alpha]_D^{26}$ −77.2° ($c$=0.8, MeOH); UV $\lambda_{max}$ (MeOH) nm (log $\varepsilon$): 276 (3.28), 225 (4.10). FAB-MS $m/z$: 679 $[M+Na]^+$. HR-FAB-MS $m/z$: 679.2196 $[M+Na]^+$ ($C_{30}H_{40}O_{16}Na$, Calcd for 679.2214). $^1$H-NMR (400 MHz, $CD_3OD$) $\delta$: 7.43 (1H, d, $J$=1.5 Hz, 3-H), 7.04 (2H, d, $J$=8.5 Hz, 2‴, 6‴-H), 6.71 (2H, d, $J$=8.5, Hz, 3‴, 5‴-H), 5.58 (1H, d, $J$=3.2 Hz, 1-H), 4.70 (1H, d, $J$=8.1 Hz, 1′-H), 4.40 (1H, d, $J$=7.8 Hz, 1″-H), 4.26, 4.25 (each 1H, t, $J$=6.8 Hz, $\alpha$-$H_2$), 3.94 (1H, dd, $J$=12.0, 2.3 Hz, 6′-$H_B$), 3.88 (1H, dd, $J$=11.8, 2.0 Hz, 6″-$H_B$), 3.84 (1H, dd, $J$=12.0, 4.4 Hz, 6′-$H_A$), 3.65 (1H, dd, $J$=11.8, 5.5 Hz, 6″-$H_A$), 3.55 (1H, m, 4′-H), 3.53 (1H, m, 3′-H), 3.46 (1H, ddd, $J$=9.3, 4.4, 2.3 Hz, 5′-H), 3.22—3.38 (6H, m, 5-H, 2′-H, 2″, 3″, 4″, 5″-H), 2.84 (2H, t, $J$=6.8 Hz, $\beta$-$H_2$), 2.56 (1H, dd, $J$=19.3, 8.3 Hz, 6-H$\beta$), 2.43 (1H, dd, $J$=19.3, 1.7 Hz, 6-H$\alpha$), 2.32 (1H, ddd, $J$=10.1, 7.3, 3.2 Hz, 9-H), 2.10 (1H, dq, $J$=10.1, 7.1 Hz, 8-H), 1.14 (3H, d, $J$=7.1 Hz, 10-$H_3$). $^{13}$C-NMR (100 MHz, $CD_3OD$): Table 2.

**Determination of Absolute Structures of Glucosyl Moieties in 1—6** Each of compounds **1**—**6** (*ca.* 1 mg) was refluxed with 4% HCl for 4 h. The

Table 1. $^{13}$C-NMR Spectral Data for **1**, **2** and **3** (100 MHz, $CD_3OD$)

| | (8*E*)-Ligstroside | **1** (8*Z*)-Ligstroside | **2** (8*E*)-Nüzhenide | **3** (8*Z*)-Nüzhenide |
|---|---|---|---|---|
| C-1 | 95.2 | 93.7 | 95.2 | 93.7 |
| C-3 | 155.2 | 154.2 | 155.2 | 154.2 |
| C-4 | 109.5 | 112.3 | 109.5 | 112.2 |
| C-5 | 31.9 | 33.6 | 31.8 | 33.6 |
| C-6 | 41.3 | 37.8 | 41.4 | 37.7 |
| C-7 | 173.2 | 173.8 | 173.1 | 173.6 |
| C-8 | 124.9 | 126.1 | 125.0 | 126.2 |
| C-9 | 130.1 | 132.2 | 130.6 | 132.1 |
| C-10 | 13.6 | 13.4 | 13.8 | 13.5 |
| C-11 | 168.7, 51.9 | 168.6, 51.8 | 168.7, 52.0 | 168.6, 51.8 |
| C-1′ | 100.9 | 100.1 | 100.9 | 100.1 |
| C-2′ | 74.8 | 74.7 | 74.8 | 74.7 |
| C-3′ | 78.0 | 78.1 | 77.98 | 78.0 |
| C-4′ | 71.5 | 71.6 | 71.6 | 71.6 |
| C-5′ | 78.5 | 78.4 | 78.5 | 78.4 |
| C-6′ | 62.8 | 62.8 | 62.8 | 62.8 |
| C-$\alpha$ | 66.9 | 66.7 | 72.3 | 72.3 |
| C-$\beta$ | 35.2 | 35.2 | 36.5 | 36.5 |
| C-1″ | 130.6 | 130.1 | 130.8 | 130.8 |
| C-2″ | 131.0 | 131.0 | 131.0 | 131.0 |
| C-3″ | 116.3 | 116.3 | 116.2 | 116.2 |
| C-4″ | 157.1 | 157.1 | 156.9 | 156.9 |
| C-5″ | 116.3 | 116.3 | 116.2 | 116.2 |
| C-6″ | 131.0 | 131.0 | 131.0 | 131.0 |
| C-1‴ | — | — | 104.5 | 104.5 |
| C-2‴ | — | — | 75.0 | 75.0 |
| C-3‴ | — | — | 78.02 | 78.1 |
| C-4‴ | — | — | 71.7 | 71.6 |
| C-5‴ | — | — | 75.2 | 75.4 |
| C-6‴ | — | — | 65.1 | 64.8 |

Table 2. $^{13}$C-NMR Spectral Data for **4**, **5** and **6** ($CD_3OD$)

| | Syringopicroside | **4** (150 MHz) | **5** (150 MHz) | **6** (100 MHz) |
|---|---|---|---|---|
| C-1 | 95.5 | 96.0 | 95.6 | 95.5 |
| C-3 | 153.2 | 153.3 | 153.2 | 153.2 |
| C-4 | 111.3 | 111.3 | 111.3 | 111.3 |
| C-5 | 28.3 | 28.5 | 28.3 | 28.3 |
| C-6 | 43.6 | 43.7 | 43.5 | 43.5 |
| C-7 | 220.7 | 220.9 | 220.7 | 220.7 |
| C-8 | 44.7 | 44.8 | 44.7 | 44.7 |
| C-9 | 46.6 | 46.6 | 46.6 | 46.6 |
| C-10 | 13.7 | 14.0 | 13.7 | 13.7 |
| C-11 | 168.4 | 168.4 | 168.4 | 168.4 |
| C-1′ | 100.3 | 100.7 | 100.0 | 100.1 |
| C-2′ | 74.7 | 74.6 | 75.6 | 75.0 |
| C-3′ | 78.1 | 78.1 | 87.5 | 76.4 |
| C-4′ | 71.6 | 71.6 | 70.1 | 80.6 |
| C-5′ | 78.5 | 76.8 | 78.24 | 77.0 |
| C-6′ | 62.8 | 68.0 | 62.7 | 61.8 |
| C-1″ | — | 100.2 | 105.2 | 104.7 |
| C-2″ | — | 73.7 | 74.1 | 74.4 |
| C-3″ | — | 75.3 | 77.9 | 77.9 |
| C-4″ | — | 71.8 | 71.6 | 71.4 |
| C-5″ | — | 73.8 | 78.16 | 78.2 |
| C-6″ | — | 62.7 | 62.7 | 62.5 |
| C-$\alpha$ | 66.3 | 66.4 | 66.4 | 66.4 |
| C-$\beta$ | 35.4 | 35.4 | 35.4 | 35.4 |
| C-1‴ | 130.2 (C-1″) | 130.2 | 130.2 | 130.2 |
| C-2‴ | 131.0 (C-2″) | 131.0 | 131.0 | 131.0 |
| C-3‴ | 116.4 (C-3″) | 116.3 | 116.4 | 116.4 |
| C-4‴ | 157.2 (C-4″) | 157.1 | 157.1 | 157.1 |
| C-5‴ | 116.4 (C-5″) | 116.3 | 116.4 | 116.4 |
| C-6‴ | 131.0 (C-6″) | 131.0 | 131.0 | 131.0 |

reaction mixture was neutralized with $Ag_2O$, filtered and excess $Ag^+$ of the filtrate was removed with $H_2S$. 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.[12] GLC conditions: column, G-column (Kagakuhin Kensa Kyokai, 1.2 mm i.d.×40 m); column temp., 240 °C; carrier gas, $N_2$ (30 ml/min). D-glucose, $t_R$ 39.4 min (ref.: L-glucose, $t_R$ 41.2 min).

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**References and Notes**

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