Studies on the Constituents of *Lonicera* Species. XVII.[1] New Iridoid Glycosides of the Stems and Leaves of *Lonicera japonica* THUNB

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Received February 21, 2002; accepted April 11, 2002

Four new iridoid glycosides, named L-phenylalaninosecologanin (1), 7-*O*-(4-β-D-glucopyranosyloxy-3-methoxybenzoyl)secologanolic acid (2), 6′-*O*-(7α-hydroxyswerosyloxy)loganin (3) and (*Z*)-aldosecologanin (5), were isolated, together with a known one, newly named (*E*)-aldosecologanin (4), from the stems and leaves of *Lonicera japonica*. Their structures were established on the basis of chemical and spectral data.

Key words *Lonicera japonica*; Caprifoliaceae; iridoid glycoside

Our previous phytochemical studies of the flower buds of *Lonicera japonica* THUNB. led to the isolation of three new glycosides.[2,3] In the course of our studies on the constituents of *Lonicera* species, we have now examined the stems and leaves ("nindou" in Japanese) of *L. japonica*, which has been used in China as an herbal drug for its antipyretic, deoxicant, diuretic and antiinflammatory effects.[4] This paper describes the structural elucidation of four new iridoid glycosides and a known one from the stems and leaves of *L. japonica*. The isolation procedure is described in detail in the experimental section.

Compound **1** was obtained as an amorphous powder, $[\alpha]_D^{26}$ −112.4° (MeOH). The molecular formula of **1**, $C_{26}H_{35}NO_{11}$, was confirmed by high-resolution (HR)-FAB-MS. Acid hydrolysis of **1** gave D-glucose, which was identified by gas-liquid chromatography (GLC) after conversion to the TMSi ether of a thiazolidine derivative.[5] Its ^{1}H- and ^{13}C-NMR spectra exhibited signals typical of a secologanin unit, but, lacked a signal due to an aldehyde (7-CHO) of secologanin and instead showed a methylene signal [δ_H 2.88 (1H, ddd, J=12.2, 9.8, 5.4 Hz), 3.03 (1H, ddd, J=12.2, 9.5, 6.3 Hz), δ_C 46.9] for 7-CH_2. Furthermore, the ^{13}C-NMR spectrum of **1** showed signals of a mono-substituted benzene ring, a carboxyl carbon (δ_C 172.6), a methylene (δ_C 37.6) and a methine (δ_C 64.9) moiety. Detailed analyses of the ^{1}H- and ^{13}C-NMR spectra of **1** were undertaken with the aid of ^{1}H–^{1}H shift correlation spectroscopy (^{1}H–^{1}H COSY) and ^{1}H-detected multiple-bond connectivity (HMBC, Fig. 1) experiments. These data and the nuclear Overhauser enhancement spectroscopy (NOESY) correlations between 1-H/8-H and 5-H/9-H suggested that **1** was an N-alkylated α-amino acid-secoiridoid conjugate, in which phenylalanine bonded to the C-7 methylene of secologanin. In order to determine the stereochemistry at the C-α of **1**, we carried out syntheses of N-alkylated amino acid-secoiridoid conjugate isomers using reductive amination of L- and D-phenylalanine with secologanin in the presence of $NaBH_3CN$, respectively.[6] The absolute configuration at C-α of the phenylalanine moiety in **1** was assigned as *S* (L-type) by comparison of the ^{1}H-NMR chemical shifts and $[\alpha]_D$ with those of the synthetic conjugates. Consequently, the structure of **1** was elucidated as shown and termed L-phenylalaninosecologanin. This is the first finding of a naturally occurring N-alkylated α-amino acid-iridoid conjugate.

Compound **2** was obtained as an amorphous powder, $[\alpha]_D^{26}$ −96.4° (MeOH). The molecular formula of **2**, $C_{30}H_{40}O_{18}$, was confirmed by HR-FAB-MS. On acid hydrolysis, D-glucose was detected as the sugar moiety of **2**. The ^{1}H- and ^{13}C-NMR spectra of **2** were similar to those of 7-(3-β-glucopyranosyloxy-2-hydroxybenzoyl) secologanol, which was isolated from *Gentiana depressa*;[7] however, it lacked a signal for the methoxyl group attached at the C-11 carbonyl in 7-(3-β-glucopyranosyloxy-2-hydroxybenzoyl) secologanol and instead showed a signal characteristic of a phenolic methoxyl group [δ_H 3.91 (3H, s), δ_C 56.8] in **2**. The major differences between the two were the chemical shifts and spin systems of the aromatic proton signals [δ_H 7.64 (1H, dd, J=8.4, 2.0 Hz), 7.61 (1H, d, J=2.0 Hz), 7.21 (1H, d, J=8.4 Hz)]. Detailed analyses of the ^{1}H- and ^{13}C-NMR spectra of **2** were undertaken with the aid of ^{1}H–^{1}H COSY and HMBC (Fig. 1) experiments. From the above data and the NOESY correlations (1-H/8-H, 5-H/9-H, 3″-OCH_3/2″-H, 1‴-H/5″-H), the structure of **2** was elucidated as shown and termed 7-*O*-(4-β-D-glucopyranosyloxy-3-methoxybenzoyl) secologanolic acid.

Compound **3** was obtained as an amorphous powder, $[\alpha]_D^{26}$ −150.7° (MeOH). The molecular formula of **3**, $C_{33}H_{46}O_{19}$, was confirmed by HR-FAB-MS. On acid hydrolysis, D-glucose was detected as the sugar moiety of **3**. Its ^{1}H-NMR spectrum showed two sets of signals, one set similar to loganin (Lo)[8] and another to sweroside (Sw),[8] indicating a dimeric structure. However, the ^{1}H-NMR spectrum of **3** lacked a signal from the C-7 oxymethylene group of sweroside and instead showed an acetal methine signal [δ_H 5.48 (1H, dd, J=9.7, 2.6 Hz)] for 7_{sw}-H. Other chemical shifts, except for signals due to the glucosyl moieties, were coincident with those of loganin and sweroside. The ^{13}C-NMR spectrum of **3** contained a set of signals almost identical to those assigned to sweroside, except for the signal due to C-7 described above. The other set of signals, corresponding to loganin, were coincident, except for the difference in chemical shift at the C_{Lo}-6′ of the β-D-glucopyranosyl (δ_C 70.6, +7.8 ppm). Detailed analyses of the ^{1}H- and ^{13}C-NMR spectra of **3** were undertaken with the aid of ^{1}H–^{1}H COSY and HMBC (Fig. 1) experiments, and the planar structure of **3** was established as shown in the chart. Furthermore, the observation of a NOESY correlation between 5_{Sw}-H and 7_{Sw}-H suggested that these protons were on the same face (α). From the above data and the NOESY correlations (1_{Lo}-H/8_{Lo}-H, 5_{Lo}-H/9_{Lo}-H, 7_{Lo}-H/8_{Lo}-H, 1_{Sw}-H/8_{Sw}-H, 5_{Sw}-H/9_{Sw}-H), the structure of **3** was elucidated as shown, and termed 6′-*O*-

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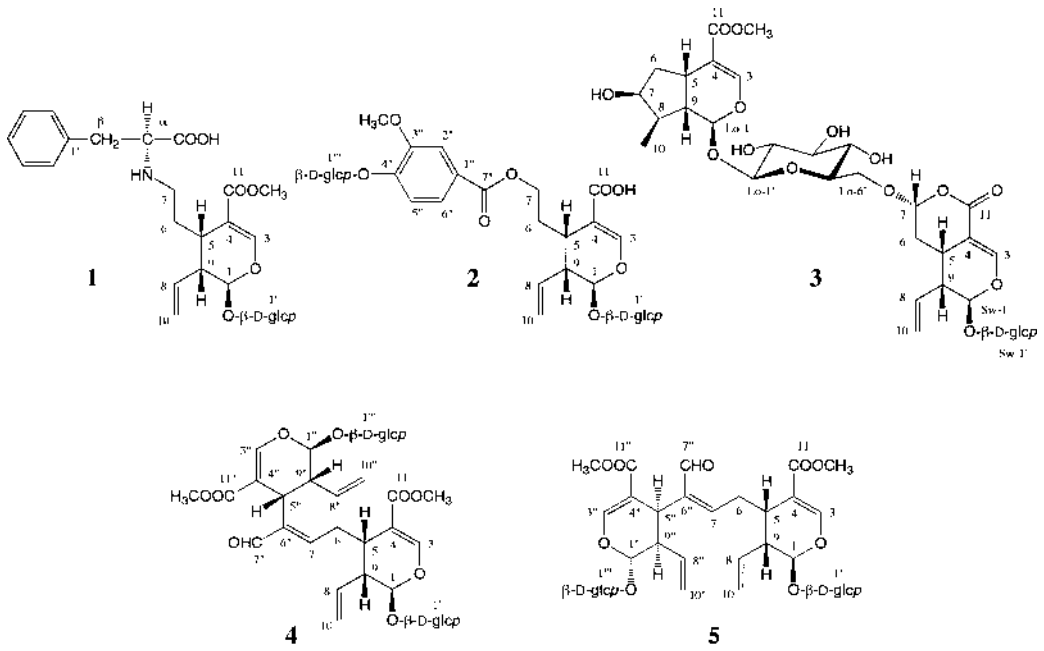

Chart 1

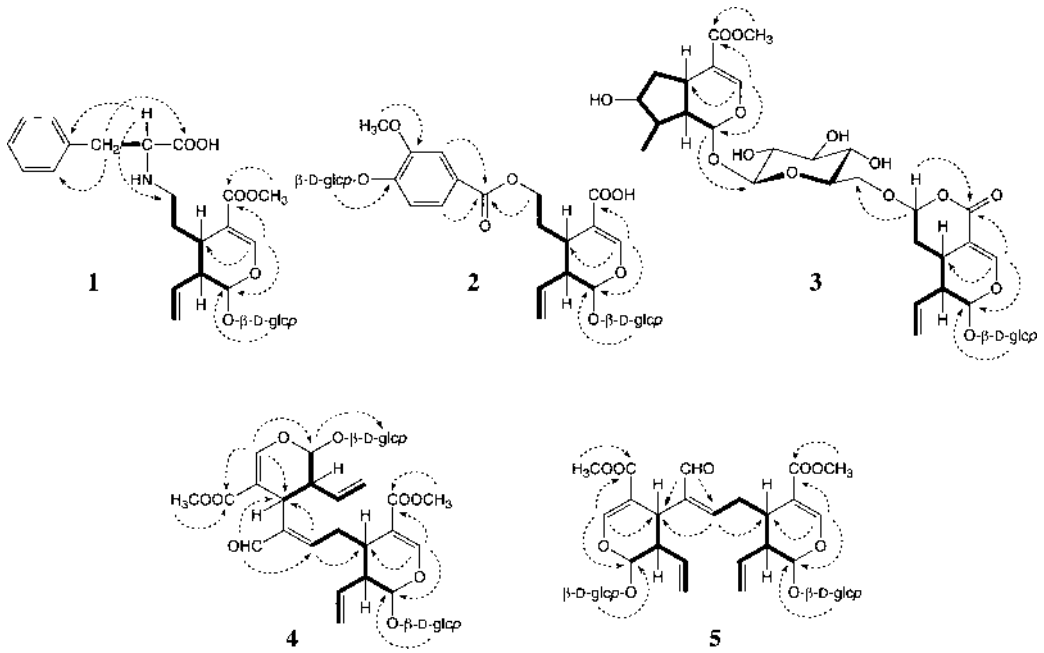

Fig. 1. The Main HMBC Correlations of **1**—**5**

Heavy lines indicated partial structures inferred from ^{1}H–^{1}H COSY.

(7α-hydroxyswerosyloxy)-loganin.

Compound **4** was obtained as an amorphous powder, $[\alpha]_D^{26}$ −135.6° (MeOH). The molecular formula of **4**, $C_{34}H_{46}O_{19}$, was confirmed by HR-FAB-MS. On acid hydrolysis, D-glucose was detected as the sugar moiety of **4**. The ^{1}H- and ^{13}C-NMR spectra of **4** showed two characteristic sets of signals for vinyl (8, 8″-H, 10, 10″-H_2), olefin (3, 3″-H), anomeric (1′, 1‴-H) and carbomethoxyl (11, 11″-$COOCH_3$) protons, indicating that **4** was a dimer of secoiridoid glycoside. The NMR spectra also exhibited signals of an aldehyde [δ_H 9.22 (1H, s), δ_C 197.1] and tri-substituted olefin [δ_H 6.71 (1H, dd, J=7.3, 6.6 Hz), δ_C 143.3 (s), 157.0 (d)] groups. Detailed analyses of ^{1}H- and ^{13}C-NMR spectra of **4** were undertaken with the aid of ^{1}H–^{1}H COSY, ^{1}H-detected hetronuclear multiple quantum coherence (HMQC) and HMBC (Fig. 1) experiments, and the planar structure of **4** was established as shown in the chart. Compound **5** was obtained as an amorphous powder, $[\alpha]_D^{26}$ −164.3° (MeOH). The molecular formula of **5**, $C_{34}H_{46}O_{19}$, was coincident with that of **4**. The ^{1}H- and ^{13}C-NMR spectra of **5** were similar to those of **4**, except for the chemical shifts owing to the 7″-CHO (δ_H 10.03, δ_C 192.0) and 7-H (δ_H 6.31, δ_C 150.7). The ^{1}H–^{1}H COSY and HMBC experiments of **5** made up the same plane structure as **4**, suggesting that **4** and **5** were deduced to be geometrical isomers

Table 1. ^{1}H- and ^{13}C-NMR Spectral Data of **4** and **5** (CD_3OD)

Position	**4**		**5**	
	δ_H	δ_C	δ_H	δ_C
1	5.58 d (5.1)	97.8	5.50 d (5.1)	97.7
3	7.54 s	154.3	7.48 d (1.1)	153.9
4	—	110.6	—	110.3
5	3.10 m	33.7	2.95 m	34.0
6	2.44 m 3.08 m	29.8	2.57 m 3.26 m	27.2
7	6.71 dd (7.3, 6.6)	157.0	6.31 dd (8.4, 8.1)	150.7
8	5.79 m	135.6[a)]	5.73 ddd (17.2, 10.3, 9.2)	135.6[a)]
9	2.78 br dd (8.8, 5.1)	45.5	2.61 ddd (9.2, 5.1, 4.4)	45.2
10	5.29 br d (9.9), 5.36 br d (17.2)	120.4	5.26 dd (10.3, 1.8) 5.29 br d (17.2)	120.5
11-$COOCH_3$	3.78 s[a)]	169.2, 52.0[b)]	3.70 s[a)]	168.9, 52.1[b)]
1′	4.69 d (8.1)	100.3	4.66 d (8.1)	100.3
2′	3.18 dd (9.2, 8.1)	74.8[c)]	3.17 dd (9.2, 8.1)	74.7
3′		78.1[d)]		78.1
4′	3.28—3.37 m	71.63[e)]	3.25—3.36 m	71.6[c)]
5′		78.42[f)]		78.43[d)]
6′	3.66 m 3.88 m	62.8[g)]	3.67 br d (12.9)[b)], 3.88 br d (12.9)[c)]	62.8[e)]
1″	5.49 d (3.3)	97.4	5.42 d (5.9)	97.5
3″	7.47 s	152.2	7.61 d (1.5)	154.5
4″	—	109.4	—	110.0
5″	4.06 m	31.1	4.08 br d (5.5)	34.0
6″	—	143.3	—	141.0
7″	9.22 s	197.1	10.03 s	192.0
8″	5.60 m	135.5[a)]	5.42 m	135.2[a)]
9″	2.59 m	46.5	2.67 ddd (9.2, 5.9, 5.5)	45.8
10″	5.02 br d (10.3) 5.07 br d (17.2)	119.4	5.07 dd (10.6, 1.5), 5.10 br d (17.2)	119.6
11″-$COOCH_3$	3.59 s[a)]	169.1, 51.7[b)]	3.66 s[a)]	168.7, 51.9[b)]
1‴	4.68 d (7.7)	99.9	4.69 d (8.1)	100.0
2‴	3.25 m	74.7[c)]	3.20 dd (9.2, 8.1)	74.7
3‴		78.0[d)]		78.1
4‴	3.28—3.37 m	71.55[e)]	3.25—3.36 m	71.5[c)]
5‴		78.37[f)]		78.4[d)]
6‴	3.66 m, 3.88 m	62.7[g)]	3.65 br d (12.9)[b)], 3.87 br d (12.9)[c)]	62.7[e)]

Values in parentheses are coupling constants in Hz. *a*—*g*) Assignment may be interchangeable in the vertical column.

with a C-7, 6″ double bond. The stereochemistry of the C-7, 6″ double bond in **4** and **5** was determined to be *E* and *Z* configurations, respectively, by the NOESY experiments (**4**: 7-H/7″-CHO, 6-H_B (δ_H 3.08)/5″-H. **5**: 6-H_B (δ_H 3.26)/7″-CHO). From the above data and the NOE correlations (**4**, **5**: 1-H/8-H, 1″-H/8″-H, 5-H/9-H, 5″-H/9″-H), the structures of **4** and **5** were clearly established as depicted in the formulas.

Takagi *et al.* previously reported the isolation of a bis-seco-oiridoid glycoside, named centauroside ($[\alpha]_D^{20}$ −130°), from the whole plant of *Erythraea centaurium*, and it has been assigned the structure **5** (*Z*-configuration).[9)] However, spectral data and the $[\alpha]_D$ of our glycoside having an *E*-configuration (**4**) and centauroside are almost identical. Thus, the structure of centauroside may be represented by **4** and not by **5**. Compound **4** seems to be the same compound isolated from the leaves of *L. morrowii* by Kondo *et al.* ($[\alpha]_D$ −134.4°)[10)] In this report, we treated **5** as a new compound and termed compounds **4** and **5** (*E*)- and (*Z*)-aldosecologanins, in consideration of their biosyntheses, respectively.

Experimental

General Optical rotations 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 δ (ppm) scale with 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) and Sephadex LH-20 (Pharmacia Fine Chemicals). Preparative HPLC was carried out on a Tosoh HPLC system [pump, CCPS; detector, UV-8020; column, Cosmosil 5C_{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). Analytical TLC was performed on precoated silica gel plates (Merck, 0.25 mm thickness).

Material The stems and leaves of *L. japonica* were purchased from Uchida Wakanyaku Co. (Japan).

Isolation The stems and leaves of *L. japonica* (2.5 kg) were extracted with MeOH at room temperature for 10 d. Evaporation of the solvent under reduced pressure provided the MeOH extract (223.0 g), and this extract was partitioned with AcOEt. The aqueous layer was passed through a Mitsubishi Diaion HP-20 column, and the adsorbed material was eluted with H_2O, MeOH and $CHCl_3$. The MeOH eluate-fraction from the Diaion HP-20 column was concentrated. The residue (41.2 g) was chromatographed on a silica gel column using $CHCl_3$–MeOH–H_2O (60 : 10 : 1, 30 : 10 : 1), $CHCl_3$–MeOH (1 : 1) and MeOH, and the eluate was separated into six fractions (frs. 1—6). Fraction 4 [$CHCl_3$–MeOH–H_2O (30 : 10 : 1) effluent, 17.0 g] was rechromatographed on a Sephadex LH-20 (25% and 50% MeOH in H_2O, and MeOH) column, and the eluate was separated into three fractions [frs. 4-1, 4-2 (12.5 g), 4-3]. Fr. 4-2 (50% MeOH effluent, 2.8 g) was subjected to

prep. HPLC [Cosmosil 5C_{18}-AR column; MeOH–H_2O (1 : 2), 233 nm, column temp., 40 °C] to give crude **1**—**5**, which was purified by prep. HPLC [Cosmosil 5SL column; CH_2Cl_2–MeOH–H_2O (30 : 10 : 1), 225 nm, flow rate: 1.5 ml/min, column temp., 26 °C] to give **1** (5.5 mg), **2** (4.5 mg), **3** (3.0 mg), **4** (35.0 mg) and **5** (1.4 mg), respectively.

L-Phenylalaninosecologanin (**1**): An amorphous powder, $[\alpha]_D^{26}$ −112.4° (c=0.214, MeOH); UV λ_{max} (MeOH) nm (log ε): 234 (4.05), 209 (3.99). FAB-MS *m/z*: 538 $[M+H]^+$. HR-FAB-MS *m/z*: 538.2308 $[M+H]^+$ ($C_{26}H_{36}NO_{11}$, Calcd for 538.2288). ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.50 (1H, d, J=0.7 Hz, 3-H), 7.33 (4H, m, 2″, 3″, 5″, 6″-H), 7.27 (1H, m, 4″-H), 5.71 (1H, ddd, J=17.2, 10.2, 8.5 Hz, 8-H), 5.51 (1H, d, J=6.6 Hz, 1-H), 5.29 (1H, br d, J=17.2 Hz, 10-H_B), 5.26 (1H, dd, J=10.2, 1.1 Hz, 10-H_A), 4.67 (1H, d, J=7.8 Hz, 1′-H), 3.90 (1H, dd, J=12.0, 2.0 Hz, 6′-H_B), 3.74 (1H, dd, J=7.4, 5.5 Hz, α-H), 3.69 (3H, s, 11-$COOCH_3$), 3.64 (1H, dd, J=12.0, 6.1 Hz, 6′-H_A), 3.24—3.38 (4H, m, β-H_B, 3′, 4′, 5′-H), 3.18 (1H, dd, J=9.3, 7.8 Hz, 2′-H), 3.10 (1H, dd, J=14.5, 7.4 Hz, β-H_A), 3.03 (1H, ddd, J=12.2, 9.5, 6.3 Hz, 7-H_B), 2.88 (1H, ddd, J=12.2, 9.8, 5.4 Hz, 7-H_A), 2.65 (1H, m, 5-H), 2.57 (1H, m, 9-H), 1.85 (2H, m, 6-H_2). ^{13}C-NMR (100 MHz, CD_3OD) δ: 172.6 (COOH), 169.3 (11-$\underline{C}OOCH_3$), 154.5 (C-3), 137.1 (C-1″), 134.9 (C-8), 130.5, 130.0 (C-2″, 3″, 5″, 6″), 128.5 (C-4″), 120.4 (C-10), 110.1 (C-4), 100.3 (C-1′), 97.5 (C-1), 78.6 (C-5′), 78.1 (C-3′), 74.7 (C-2′), 71.4 (C-4′), 64.9 (C-α), 62.9 (C-6′), 52.0 (11-COO$\underline{C}H_3$), 46.9 (C-7), 45.3 (C-9), 37.6 (C-β), 32.1 (C-5), 27.9 (C-6).

Syntheses of L-Phenylalaninosecologanin (1) and D-One A solution of secologanin (50.0 mg, 0.13 mmol) in MeOH (3 ml) was treated with L-phenylalanine (30.0 mg, 0.18 mmol) in the presence of $NaBH_3CN$ (20.0 mg, 0.32 mmol), and the mixture was stirred at room temp. for 20 h. The reaction mixture was filtered and the filtrate was evaporated under reduced pressure. The residue was purified by HPLC [Cosmosil 5C_{18}-AR column; MeOH–H_2O (2 : 3), 233 nm, column temp., 40 °C, flow rate: 1.5 ml/min] to give synthetic **1** (L-form, 19.5 mg, 27.7%; t_R 16.7 min). On the other hand, secologanin (50.0 mg, 0.13 mmol) in MeOH (3 ml) was treated with D-phenylalanine (30.0 mg, 0.18 mmol) in the presence of $NaBH_3CN$ (20.0 mg, 0.32 mmol) described for synthetic **1**, above, to provide the synthetic D-form (18.8 mg, 26.9%; t_R 17.3 min). Synthetic **1** (L-form), $[\alpha]_D^{26}$ −114.2° (c=0.972, MeOH). The ^{1}H-NMR spectral data was identical with that of **1**. Synthetic D-form, $[\alpha]_D^{26}$ −125.7° (c=0.945, MeOH). ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.50 (1H, s, 3-H), 7.31 (5H, m, 2″, 3″, 5″, 6″-H), 7.25 (1H, m, 4″-H), 5.73 (1H, ddd, J=17.3, 10.5, 8.4 Hz, 8-H), 5.51 (1H, d, J=7.1 Hz, 1-H), 5.30 (1H, br d, J=17.3 Hz, 10-H_B), 5.26 (1H, br d, J=10.5 Hz, 10-H_A), 4.67 (1H, d, J=7.8 Hz, 1′-H), 3.90 (1H, dd, J=12.0, 2.0 Hz, 6′-HB), 3.67 (3H, s, 11-$COOCH_3$), 3.65 (2H, m, α-H, 6′-H_A), 3.23—3.37 (4H, m, β-H_B, 3′, 4′, 5′-H), 3.18 (1H, dd, J=9.0, 7.8 Hz, 2′-H), 3.08 (1H, dd, J=14.6, 7.2 Hz, β-H_A), 2.90 (2H, m, 7-H_2), 2.78 (1H, m, 5-H), 2.60 (1H, m, 9-H), 1.86 (2H, m, 6-H_2).

7-*O*-(4-β-D-Glucopyranosyloxy-3-methoxybenzoyl)secologanolic Acid (**2**): An amorphous powder, $[\alpha]_D^{26}$ −96.4° (c=0.149, MeOH); UV λ_{max} (MeOH) nm (log ε): 289 (3.56), 243 (4.02), 214 (4.28), 203 (3.26). FAB-MS *m/z*: 711 $[M+Na]^+$. HR-FAB-MS *m/z*: 711.2134 $[M+Na]^+$ ($C_{30}H_{40}O_{18}Na$, Calcd for 711.2113). ^{1}H-NMR (400 MHz, CD_3OD) δ: 7.64 (1H, dd, J=8.4, 2.0 Hz, 6″-H), 7.61 (1H, d, J=2.0 Hz, 2″-H), 7.46 (1H, s, 3-H), 7.21 (1H, d, J=8.4 Hz, 5″-H), 5.83 (1H, ddd, J=17.6, 10.2, 8.8 Hz, 8-H), 5.56 (1H, d, J=6.3 Hz, 1-H), 5.31 (1H, br d, J=17.6 Hz, 10-H_B), 5.26 (1H, br d, J=10.2 Hz, 10-H_A), 5.02 (1H, d, J=7.3 Hz, 1‴-H), 4.70 (1H, d, J=7.8 Hz, 1′-H), 4.35 (2H, m, 7-H_2), 3.91 (3H, s, 3″-OCH_3), 3.87 (2H, m, 6′, 6‴-H_B), 3.67 (2H, m, 6′, 6‴-H_A), 2.98 (1H, m, 5-H), 2.70 (1H, m, 9-H), 2.19 (1H, m, 6-H_B), 1.94 (1H, m, 6-H_A). ^{13}C-NMR (100 MHz, CD_3OD) δ: 167.8 (C-7″), 152.2 (C-4″), 150.5 (C-3″), 136.0 (C-8), 125.7 (C-1″), 124.7 (C-6″), 119.5 (C-10), 116.5 (C-5″), 114.3 (C-2″), 102.0 (C-1‴), 100.2 (C-1′), 97.7 (C-1), 78.5, 78.4, 78.1, 78.0 (C-3′, 3‴, 5′, 5‴), 74.8, 74.7 (C-2′, 2‴), 71.7, 71.3 (C-4′, 4‴), 64.8 (C-7), 62.9, 62.5 (C-6′, 6‴), 56.8 (3″-OCH_3), 45.5 (C-9), 31.4 (C-5), 30.2 (C-6). 11-COOH, C-3 and C-4 were not detected directly from the ^{13}C-NMR spectrum, but the chemical shifts were obtained approximately from the HMBC spectrum [*ca.* 170.1 (11-COOH), *ca.* 153.8 (C-3), *ca.* 112.5 (C-4)].

6′-*O*-(7α-Hydroxyswerosyloxy)loganin (**3**): An amorphous powder, $[\alpha]_D^{26}$ −150.7° (c=0.146, MeOH); UV λ_{max} (MeOH) nm (log ε): 236 (4.23). FAB-MS *m/z*: 769 $[M+Na]^+$. HR-FAB-MS *m/z*: 769.2498 $[M+Na]^+$ ($C_{33}H_{46}O_{19}Na$, Calcd for 769.2532). ^{1}H-NMR (600 MHz, CD_3OD) δ: 7.59 (1H, d, J=2.6 Hz, 3_{Sw}-H), 7.40 (1H, d, J=1.1 Hz, 3_{Lo}-H), 5.56 (1H, d, J=1.8 Hz, 1_{Sw}-H), 5.51 (1H, ddd, J=17.6, 10.3, 9.7 Hz, 8_{Sw}-H), 5.48 (1H, dd, J=9.7, 2.6 Hz, 7_{Sw}-H), 5.30 (1H, br d, J=17.6 Hz, 10_{Sw}-H_B), 5.28 (1H, dd, J=10.3, 1.8 Hz, 10_{Sw}-H_A), 5.12 (1H, d, J=4.8 Hz, 1_{Lo}-H), 4.67 (1H, d, J=8.1 Hz, $1'_{Sw}$-H), 4.65 (1H, d, J=7.7 Hz, $1'_{Lo}$-H), 4.26 (1H, dd, J=11.4, 1.8 Hz, $6'_{Lo}$-H_B), 4.05 (1H, m, 7_{Lo}-H), 3.89 (1H, dd, J=11.7, 1.9 Hz, $6'_{Sw}$-H_B), 3.78 (1H, dd, J=11.4, 7.0 Hz, $6'_{Lo}$-H_A), 3.69 (3H, s, 11_{Lo}-$COOCH_3$), 3.66 (1H, dd, J=11.7, 5.9 Hz, $6'_{Sw}$-H_A), 3.49 (1H, ddd, J=9.9, 7.0, 1.8 Hz, $5'_{Lo}$-H), 3.11 (1H, m, 5_{Lo}-H), 3.09 (1H, m, 5_{Sw}-H), 2.66 (1H, br dd, J=9.7, 5.9 Hz, 9_{Sw}-H), 2.25 (1H, br dd, J=13.9, 7.7 Hz, 6_{Lo}-Hβ), 2.01 (2H, m, 9_{Lo}-H, 6_{Sw}-Hβ), 1.87 (1H, m, 8_{Lo}-H), 1.55 (2H, m, 6_{Lo}-Hα, 6_{Sw}-Hα), 1.09 (3H, d, J=7.0 Hz, 10_{Lo}-H_3). ^{13}C-NMR (150 MHz, CD_3OD) δ: 169.5 (C_{Lo}-$\underline{C}OOCH_3$), 167.6 (C_{Sw}-11), 154.2 (C_{Sw}-3), 152.3 (C_{Lo}-3), 133.1 (C_{Sw}-8), 121.2 (C_{Sw}-10), 114.0 (C_{Lo}-4), 105.1 (C_{Sw}-4, 7), 100.5 (C_{Lo}-1′), 99.8 (C_{Sw}-1′), 98.4 (C_{Lo}-1), 98.0 (C_{Sw}-1), 78.5 (C_{Sw}-5′), 78.1 (C_{Lo}-3′, C_{Sw}-3′), 77.0 (C_{Lo}-5′), 75.0 (C_{Lo}-7), 74.7 (C_{Lo}-2′, C_{Sw}-2′), 71.8 (C_{Lo}-4′), 71.6 (C_{Sw}-4′), 70.6 (C_{Lo}-6′), 62.7 (C_{Sw}-6′), 51.7 (C_{Lo}-COO$\underline{C}H_3$), 46.6 (C_{Lo}-9), 43.9 (C_{Sw}-9), 43.0 (C_{Lo}-6), 42.4 (C_{Lo}-8), 32.4 (C_{Lo}-5), 31.8 (C_{Sw}-6), 25.3 (C_{Sw}-5), 13.7 (C_{Lo}-10).

(*E*)-Aldosecologanin (**4**): An amorphous powder, $[\alpha]_D^{26}$ −135.6° (c=0.295, MeOH); UV λ_{max} (MeOH) nm (log ε): 233 (4.46). FAB-MS *m/z*: 781 $[M+Na]^+$. HR-FAB-MS *m/z*: 781.2546 $[M+Na]^+$ ($C_{34}H_{46}O_{19}Na$, Calcd for 781.2531). ^{1}H- (600 MHz) and ^{13}C-NMR (150 MHz): Table 1.

(*Z*)-Aldosecologanin (**5**): An amorphous powder, $[\alpha]_D^{26}$ −164.3° (c=0.141, MeOH); UV λ_{max} (MeOH) nm (log ε): 232 (4.06). FAB-MS *m/z*: 781 $[M+Na]^+$. HR-FAB-MS *m/z*: 781.2546 $[M+Na]^+$ ($C_{34}H_{46}O_{19}Na$, Calcd for 781.2531). ^{1}H- (600 MHz) and ^{13}C-NMR (150 MHz): Table 1.

Determination of Absolute Structures of Glucosyl Moieties in 1—5 Each of compounds **1**—**5** (*ca.* 1 mg) was refluxed with 4% HCl for 4.5 h. The reaction mixture was neutralized with Ag_2O, filtered and the excess Ag^+ in 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.[5] 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).

Ackowledgements The authors are grateful to Mrs. S. Sato and T. Matsuki of their university for NMR and MS measurements.

References and Notes

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