Five New Steroidal Glycosides from the Stems of *Solanum sodomaeum*

Masateru ONO,*[,a] Yuuki UENOSONO,[a] Hideharu UMAOKA,[a] Yuki SHIONO,[a] Tsuyoshi IKEDA,[b] Masafumi OKAWA,[c] Junei KINJO,[c] Hitoshi YOSHIMITSU,[d] and Toshihiro NOHARA[d]

[a] *School of Agriculture, Tokai University; 5435 Minamiaso, Aso, Kumamoto 869–1404, Japan:* [b] *Faculty of Medical and Pharmaceutical Sciences, Kumamoto University; 5–1 Oe-honmachi, Kumamoto 862–0973, Japan:* [c] *Faculty of Pharmaceutical Sciences, Fukuoka University; 8–19–1 Nanakuma, Jonan-ku, Fukuoka 814–0180, Japan: and* [d] *Faculty of Pharmaceutical Sciences, Sojo University; 4–22–1 Ikeda, Kumamoto 860–0082, Japan.*
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Besides 12 known glycosides, five new steroidal glycosides have been isolated from the stems of *Solanum sodomaeum* L. (Solanaceae). The chemical structures of these five glycosides were determined on the basis of spectroscopic data as well as chemical evidence, and the structure of one known steroidal glycoside was corrected.

Key words *Solanum sodomaeum*; Solanaceae; steroidal glycoside; pregnane alkaloid; furostanol glycoside

Solanum sodomaeum L. is a solanaceous plant native to the Libyan Desert. There exist reports on the antineoplastic activity of a mixture of glycoalkaloids extracted from the fruits of this plant against Sarcoma 180 in mice.[1)] Furthermore, it has been reported that a cream formulation containing purified glycoalkaloids isolated from the fruits was effective in the treatment of malignant human skin tumors; basal cell carcinomas, squamous cell carcinomas, and benign tumors; and keratoses and keratoacanthomas.[2)] Fruit constituents such as steroidal glycosides and pyrrole alkaloids were also studied.[3,4)] In the preceding paper, we had reported the isolation and structural elucidation of eight steroidal glycosides obtained from the methanol (MeOH) extract of the underground parts of this plant. Additionally, we had reported on the antiproliferative activity of these eight steroidal glycosides against human promyelocytic leukemia (HL-60) cells.[5)] As a continuation to this study, we now describe the isolation and structural elucidation of 5 new steroidal glycosides obtained from the MeOH extract of the stems of *S. sodomaeum* L., along with 12 known glycosides. In the process, the structure of one of these glycosides was corrected.

The MeOH extract of the stems of *S. sodomaeum* was suspended in H_2O and extracted with ethyl acetate (EtOAc). The aqueous layer was partitioned between H_2O and *n*-butanol (BuOH). The BuOH soluble fraction was then subjected to silica gel, Chromatorex octadecyl silica (ODS), and Diaion HP20 column chromatography and HPLC on ODS to afford 17 glycosides (**1**—**17**).

Compounds **7**—**17** were identified as Pd (**7**),[5)] abutiloside O (**8**),[5)] solamargine (**9**),[5)] solasonine (**10**),[6)] sycophantine (**11**),[6)] protodioscin (**12**),[5)] anguivioside XV (**13**),[7)] solasodoside A (**14**),[5)] γ-methyl-δ-hydroxy pentanoic acid glucoside (**15**),[8)] methyl γ-methyl-δ-hydroxy pentanoate glucoside (**16**),[9)] and (3*S*,6*E*)-8-hydroxylinalool 3-*O*-β-D-glucopyranoside (**17**),[10)] respectively, based on the comparison of their physical and spectral data with authentic samples or those already reported (Fig. 1), although NMR spectral data of **16** and **17** have not been reported in the literature.

Compound **1**, tentatively named solasodoside B, was obtained as an amorphous powder, exhibiting an $[M+Na]^+$ ion peak at *m*/*z* 969 in the positive FAB-MS. The molecular formula of **1** was determined to be $C_{45}H_{70}O_{21}$ by high-resolution (HR)-positive FAB-MS. The IR spectrum of **1** displayed strong absorption bands at 3415 cm^{-1} due to hydroxyl groups and at 1768 cm^{-1} due to γ-lactone group. The ^{1}H-NMR spectrum of **1** exhibited signals corresponding to three tertiary methyl groups (δ 1.83, 1.02, 0.86), one olefinic proton [δ 5.31 (br d, J=4.5 Hz)], and four anomeric protons [δ 6.39 (s), 5.97 (s), 5.22 (d, J=7.5 Hz), 4.97 (d, J=7.5 Hz)]. The ^{13}C-NMR spectrum of **1** showed 45 carbon signals, including those corresponding to one carbonyl carbon (δ 179.0), two olefinic carbons (δ 140.9, 121.5), one oxygenated quaternary carbon (δ 74.4), and four anomeric carbons (δ 107.6, 102.0, 101.5, 100.3). These NMR signals were assigned in detail with the aid of ^{1}H–^{1}H correlation spectroscopy (COSY), heteronuclear multiple quantum coherence (HMQC), and heteronuclear multiple bond correlation (HMBC) spectra, as shown in Table 1. Thus, the planar structure of **1**, a steroidal glycoside possessing one γ-lactone ring between C-22 and C-16 and one tetraglycosyl group at C-3 of aglycone, could be determined. On acidic hydrolysis, **1** afforded L-rhamnose, D-xylose, and D-glucose, which were confirmed by optical rotation using chiral detection in HPLC analysis. The ^{1}H- and ^{13}C-NMR data of the sugar moiety and of the C-1—C-11 of the aglycone moiety of **1** were superimposable on those of **14**,[5)] indicating that the sugar chain attached to the β-hydroxyl group at C-3 of aglycone was identical to the sugar chain of **14**. The stereochemistry at C-16, C-17, and C-20 of aglycone was defined on the basis of the nuclear Overhauser and exchange spectroscopy (NOESY) spectrum, in which key nuclear Overhauser effects (NOEs) were observed between respective protons, as shown in Fig. 2. The structure of **1** was thus concluded to be 3-*O*-{α-L-rhamnopyranosyl-(1→2)-*O*-[β-D-xylopyranosyl-(1→2)-*O*-α-L-rhamnopyranosyl-(1→4)]-β-D-glucopyranosyl} (β-sycophantetraosyl)-20*S*-3β,16β,20-trihydroxy-pregn-5-en-20-carboxylic acid (22,16)-lactone. Although the aglycone of **1**, called 20*S*-hydroxyvespertilin, was previously reported,[11)] **1** is the first example of its glycoside.

Compound **2**, tentatively designated solasodoside C, was obtained as an amorphous powder. The positive FAB-MS of **2** indicated an $[M+Na]^+$ ion peak at *m*/*z* 807, and the molecular formula of **2** was determined to be $C_{39}H_{60}O_{16}$ by HR-positive FAB-MS. The ^{1}H- and ^{13}C-NMR signals of the aglycone and sugar moieties were quite similar to those of **7** and

* To whom correspondence should be addressed. e-mail: mono@agri.u-tokai.ac.jp

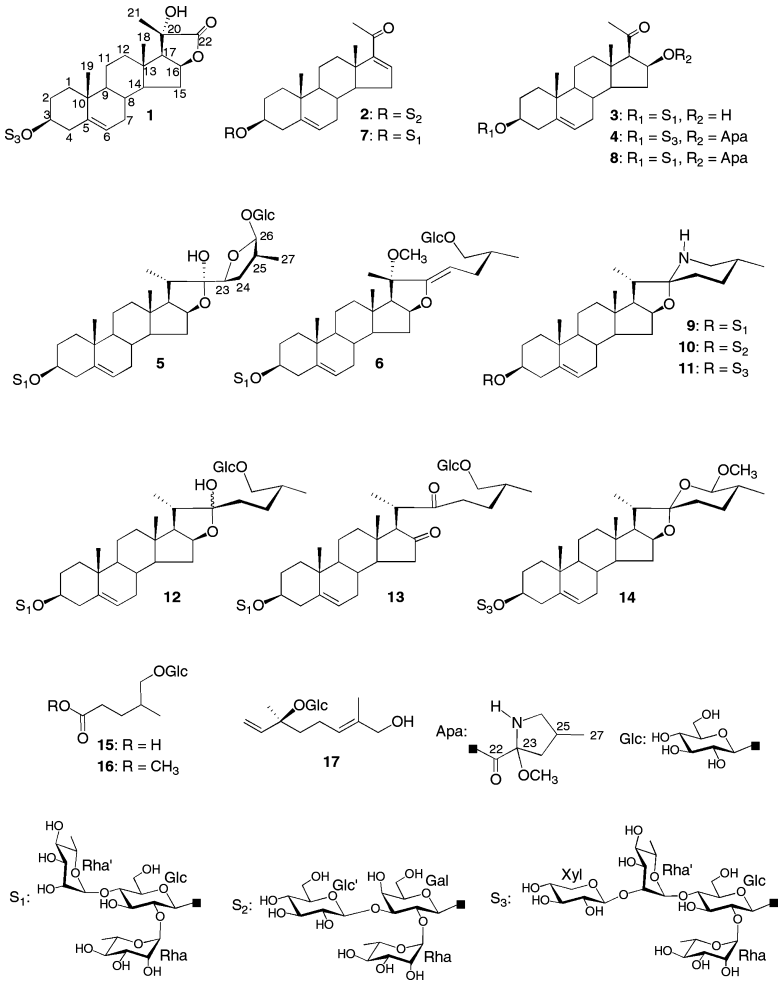

Fig. 1. Structures of **1**—**17**

10, respectively. Consequently, the structure of **2** was concluded to be 3-*O*-α-L-rhamnopyranosyl-(1→2)-*O*-[β-D-glucopyranosyl-(1→3)]-β-D-galactopyranosyl-pregna-5,16-dien-3β-ol-20-one.

Compound **3**, tentatively designated solasodoside D, exhibited an $[M+Na]^+$ ion peak at *m*/*z* 809 in the positive FAB-MS. The molecular formula of **3**, indicated by the HR-positive FAB-MS, was $C_{39}H_{62}O_{16}$. The ^{1}H-NMR spectrum of **3** gave signals due to two tertiary methyl groups (δ 1.45, 1.06), one acetyl group (δ 2.34), one olefinic proton [δ 5.34 (br d, J=5.0 Hz)], and three monosaccharide groups. These signals were similar to those of **7**; the only difference is that in the case of **7**, the signal corresponding to one olefinic proton is absent, whereas a signal corresponding to one additional oxygenated methine proton [δ 4.93 (m)] is present. Additionally, the ^{13}C-NMR spectrum of **3** was also similar to that of **7**, except for the resonances of C-12—C-21 of the aglycone moiety, which were almost same as those of 3-*O*-β-lycotetraosyl-5α-pregna-3β,16β-diol-20-one.[12] The structure of **3** was therefore defined as 3-*O*-β-chacotriosyl-pregna-5-en-3β,16β-diol-20-one.

Compound **4**, tentatively designated solasodoside E, was obtained as an amorphous powder, and its positive FAB-MS showed an $[M+Na]^+$ ion peak at *m*/*z* 1082, which was 132 mass units larger than that of **8**. The molecular formula of **4** was determined to be $C_{51}H_{81}NO_{22}$ by HR-positive FAB-MS.

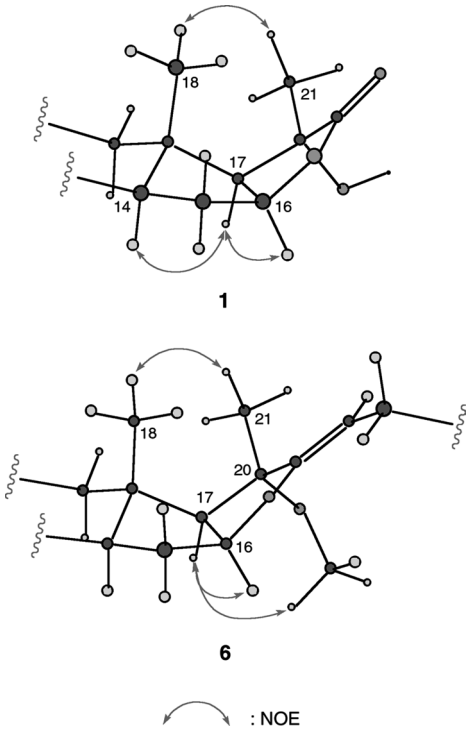

Fig. 2. Selected NOE Correlations Observed for **1** and **6** in the NOESY Spectra (in Pyridine-d_5, 500 MHz)

Table 1. ^{13}C-NMR Spectral Data for **1**—**5** (in Pyridine-d_5, 125 MHz)

	1	**2**	**3**	**4**	**5**		**1**	**2**	**3**	**4**	**5**
Ag-1	37.5	37.4	37.5	37.5	37.6	Glc-1	100.3		100.3	100.3	100.3
2	30.1	30.2	30.2	30.1	30.2	2	78.1[a)]		78.0[a)]	78.1[a)]	78.0[a)]
3	78.2	78.4	78.2	78.2	78.2	3	77.9[a)]		77.8[a)]	77.9[a)]	77.9[a)]
4	39.0	38.9	39.0	39.0	39.0	4	77.9[a)]		78.8	77.9[a)]	78.9
5	140.9	141.4	141.0	140.9	140.8	5	77.2		76.9	77.1	76.9
6	121.5	121.5	121.8	121.8	121.8	6	61.5		61.4	61.5	61.4
7	32.0	31.9	32.1	32.1	32.3	Gal-1		100.5			
8	31.1	30.4	31.3	31.4	31.8	2		76.5			
9	50.1	50.8	50.6	50.6	50.4	3		84.9			
10	37.0	37.2	37.2	37.1	37.2	4		70.4			
11	20.4	21.0	20.7	20.7	21.1	5		75.1			
12	38.8	35.2	38.7	38.3	39.8	6		62.7			
13	40.4	46.3	42.1	42.5	40.9	Glc′-1		105.9			100.7
14	56.0	56.6	54.5	54.3	56.7	2		75.0			74.7
15	32.3	32.4	38.3	37.6	32.1	3		78.5			78.9[b)]
16	82.6	144.7	71.8	74.5	81.5	4		71.7			71.6
17	64.4	155.3	69.3	67.8	64.7	5		77.6			78.7[b)]
18	13.7	16.0	14.4	14.8	16.3	6		62.6			62.7
19	19.4	19.3	19.4	19.4	19.4	Rha-1	102.0	102.2	102.0	102.0	102.0
20	74.2	196.3	208.3	206.5	39.2	2	72.5	72.6	72.5	72.5	72.5
21	20.0	27.1	30.7	31.1	16.5	3	72.9	72.9	72.8	72.8	72.8
22	179.0			167.5	109.1	4	74.2	74.2	74.2	74.1	74.2
23				97.2	85.1	5	69.5	69.5	69.5	69.5	69.5
24				40.7	32.5	6	18.6	18.6	18.6	18.6	18.6
25				26.0	40.3	Rha′-1	101.5		102.9	101.4	103.0
26				49.0	107.3	2	81.8		72.6	81.8	72.5
27				18.6	16.7	3	72.9		72.8	72.8	72.8
OCH_3				49.9		4	74.4		73.9	74.3	73.9
						5	70.0		70.5	70.0	70.5
						6	18.3		18.5	18.3	18.5
						Xyl-1	107.6			107.5	
						2	75.6			75.5	
						3	78.5			78.4	
						4	71.0			71.0	
						5	67.4			67.4	

δ in ppm from tetramethylsilane. *a*, *b*) Assignments in each column may be interchangeable. Glc, glucopyranosyl; Gal, galactopyranosyl; Rha, rhamnopyranosyl; Xyl, xylopyranosyl; Ag, aglycone moiety.

The ^{1}H- and ^{13}C-NMR signals of the aglycone moiety of **4** were superimposable on those of **8**, and the ^{1}H- and ^{13}C-NMR signals of the sugar moiety were very similar to those of **1**. Therefore, **4** was defined as 3-*O*-β-sycophantetraosyl-3β,16β-dihydroxy-pregn-5-en-20-one 16-*O*-(2,5-epimino-2-methoxy-4-pentanoic acid)-ester.

Compound **5**, tentatively designated solasodoside F, was obtained as an amorphous powder, and it exhibited an $[M+Na]^+$ ion peak at *m/z* 1085 in the positive FAB-MS; the molecular formula of **5** was found to be $C_{51}H_{82}O_{23}$ by HR-positive FAB-MS. The ^{1}H-NMR spectrum of **5** showed signals due to two tertiary methyl groups (δ 1.03, 0.92), two secondary methyl groups [δ 1.27 (d, J=6.5 Hz), 0.84 (d, J=7.5 Hz)], one olefinic proton [δ 5.30 (br d, J=3.5 Hz)], and four monosaccharide groups including a β-chacotriosyl group. The ^{13}C-NMR spectrum of **5** emitted 51 carbon signals, comprising those corresponding to two olefinic carbons (δ 140.8, 121.8), two acetal carbons (δ 109.1, 107.3), and four anomeric carbons (δ 103.0, 102.0, 100.7, 100.3). These ^{1}H- and ^{13}C-NMR signals were assigned in detail, and the planar structure of **5** was determined. The ^{13}C-NMR assignments were closely analogous to those of anguivioside XI[13]; however, the assignments revealed the replacement of the α-L-rhamnopyranosyl-(1→2)-*O*-[β-D-xylopyranosyl-(1→3)]-β-D-glucopyranosyl group attached to the β-hydroxyl group at C-3 in anguvioside XI by the β-chacotriosyl group. Consequently, the structure of **5** is defined as 3-*O*-β-chacotriosyl-26-*O*-β-D-glucopyranosyl-(22*S*,23*S*,25*R*,26*S*)-3β,22α,26-trihydroxyfurost-5-en-23,26-epoxide.

Compound **6** was identified as dioscoreside E, whose structure, based on physical and spectral data, was reported as 3-*O*-β-chacotriosyl-26-*O*-β-D-glucopyranosyl-20*R*-methoxy-25*R*-furosta-5,22(23)-diene-3β,26-diol.[14] However, in the NOESY spectrum of **6**, key NOEs were observed between H-16 and H-17, H-17 and OCH_3, and H_3-18 and H_3-21 (Fig. 2). Thus, the configuration of dioscoreside E at C-20 should be corrected as shown in Fig. 1.

To the best of our knowledge, **1**—**5** are new compounds, and the isolation of **6**, **11**, **13**, and **15**—**17** from *S. sodomaeum* L. has been described here for the first time.

Experimental

All instruments and materials used were the same as those cited in a previous report,[15] unless otherwise specified.

Plant Material The stems of *S. sodomaeum* L. were collected in the Medical Plant Garden of Kumamoto University, Kumamoto, Japan, in October 2001, and identified by one of the author (Professor Toshihiro Nohara).

Extraction and Isolation The freshly cut stems (5540 g) of *S. sodomaeum* L. were extracted with MeOH at room temperature. The solvent was then removed under reduced pressure to produce a syrup (76.0 g) which was suspended in H_2O. The suspension was then extracted with EtOAc to afford an H_2O-soluble fraction (fr.) (55.3 g) as well as an EtOAc-soluble fr.

(20.7 g). The H_2O-soluble fr. was partitioned bsetween BuOH and H_2O to give a BuOH-soluble fr. (27.9 g); this BuOH-soluble fr. was subjected to silica gel column chromatography [$CHCl_3$–MeOH–H_2O (10 : 2 : 0.1, 8 : 2 : 0.2, 7 : 3 : 0.5, 6 : 4 : 1)] to yield frs. 1—20. Chromatography of fr. 6 (267 mg) on a Chromatorex ODS column furnished frs. 6.1—6.4. HPLC [column, Cosmosil 5C18 AR-II, Nacalai Tesque, Inc., 250 mm×20 mm; solvent, 35% MeOH] of fr. 6.3 (42 mg) afforded **17** (8 mg). Fraction 10 (1348 mg) was subjected to Chromatorex ODS column chromatography (40% MeOH, 50% MeOH, 60% MeOH, 70% MeOH, 80% MeOH, MeOH) to give frs. 10.1—10.9, and **8** (112 mg). Fractions 10.3 (38 mg) and 10.4 (107 mg) were each subjected to HPLC [55% MeOH (fr. 10.3); 65% MeOH (fr. 10.4)], in the same manner as fr. 6.3, to afford **3** (6 mg) and **7** (62 mg), respectively. Furthermore, chromatography of fr. 12 (5766 mg) on a Chromatorex ODS column (65% MeOH, 75% MeOH, 85% MeOH, 95% MeOH, MeOH) furnished frs. 12.1—12.9, and **9** (716 mg). HPLC (fr. 12.3, 65% MeOH; fr. 12.8, 85% MeOH) of fr. 12.3 (170 mg) and fr. 12.8 (251 mg), conducted in a similar manner to HPLC of fr. 6.3, gave **2** (8 mg) and **14** (28 mg), respectively. Chromatorex ODS column chromatography of fr. 14 (6852 mg) gave frs. 14.1—14.17 and **10** (113 mg). Fractions 14.8 (235 mg), 14.9 (164 mg), 14.11 (786 mg), and 14.14 (507 mg) were each subjected to HPLC (fr. 14.8, 50% MeOH; fr. 14.9, 70% MeOH; fr. 14.11, 70% MeOH; fr. 14.14, 80% MeOH); the experimental conditions were similar to those during HPLC of fr. 6.3. Fraction 14.8 yielded **15** (19 mg), **16** (4 mg), and **1** (8 mg); fr. 14.9 yielded **13** (27 mg), **4** (25 mg), and **7** (14 mg); fr. 14.11 yielded **12** (30 mg); and fr. 14.14 yielded **11** (15 mg). Fraction 14.10 (1025 mg) was subsequently subjected to Diaion HP20 column chromatography (10% MeOH, 20% MeOH, 30% MeOH, 40% MeOH, 50% MeOH, 60% MeOH, 70% MeOH, 80% MeOH, 90% MeOH, MeOH, acetone) and HPLC (70% MeOH) under conditions similar to those during HPLC of fr. 6.3 to afford **6** (13 mg), **12** (70 mg), and **5** (4 mg).

1: Amorphous powder. $[\alpha]_D^{31}$ −70.0° (c=0.8, pyridine). IR (KBr) cm^{-1}: 3415 (OH), 1768 (γ-lactone). Positive FAB-MS m/z: 969 $[M+Na]^+$. HR-positive FAB-MS m/z: 969.4390 $[M+Na]^+$ (Calcd for $C_{45}H_{70}O_{21}Na$: 969.4307). ^{1}H-NMR (in pyridine-d_5, 500 MHz) δ: 6.39 (1H, s, H-1 of Rha), 5.97 (1H, s, H-1 of Rha′), 5.34 (1H, m, H-16 of Ag), 5.31 (1H, br d, J=4.5 Hz, H-6 of Ag), 5.22 (1H, d, J=7.5 Hz, H-1 of Xyl), 4.97 (1H, d, J=7.5 Hz, H-1 of Glc), 4.83 (1H, d, J=3.5 Hz, H-2 of Rha), 4.65 (1H, d, J=3.5 Hz, H-2 of Rha′), 4.63 (1H, dd, J=3.5, 9.5 Hz, H-3 of Rha), 4.53 (1H, dd, J=3.5, 9.5 Hz, H-3 of Rha′), 4.07 (1H, dd, J=7.5, 8.5 Hz, H-2 of Xyl), 3.89 (1H, m, H-3 of Ag), 2.81 (1H, br dd, J=4.0, 12.5 Hz, Ha-4 of Ag), 2.72 (1H, br dd, J=12.5, 12.5 Hz, Hb-4 of Ag), 2.34 (1H, d, J=6.5 Hz, H-17 of Ag), 1.83 (3H, s, H_3-21 of Ag), 1.77 (3H, d, J=6.5 Hz, H_3-6 of Rha), 1.57 (3H, d, J=6.5 Hz, H_3-6 of Rha′), 1.02 (3H, s, H_3-19 of Ag), 0.86 (3H, s, H_3-18 of Ag). ^{13}C-NMR data: see Table 1.

2: Amorphous powder. $[\alpha]_D^{25}$ −71.8° (c=0.9, pyridine). IR (KBr) cm^{-1}: 3446 (OH), 1647, 1585 (enone). Negative FAB-MS m/z: 783 $[M-H]^-$. Positive FAB-MS m/z: 807 $[M+Na]^+$. HR-positive FAB-MS m/z: 807.3785 $[M+Na]^+$ (Calcd for $C_{39}H_{60}O_{16}Na$: 807.3777). ^{1}H-NMR (in pyridine-d_5, 500 MHz) δ: 6.62 (1H, br s, H-16 of Ag), 6.29 (1H, s, H-1 of Rha), 5.36 (1H, br d, J=5.0 Hz, H-6 of Ag), 5.19 (1H, d, J=8.0 Hz, H-1 of Glc), 4.93 (1H, d, J=8.0 Hz, H-1 of Gal), 4.81 (1H, br d, J=3.0 Hz, H-2 of Rha), 4.69 (1H, dd, J=8.5, 9.5 Hz, H-2 of Glc), 4.60 (1H, dd, J=3.0, 9.0 Hz, H-3 of Rha), 4.38 (1H, dd, J=6.5, 11.0 Hz, Ha-6 of Gal), 2.82 (1H, br dd, J=3.5, 12.0 Hz, Ha-4 of Ag), 2.75 (1H, br dd, J=12.0, 12.0 Hz, Hb-4 of Ag), 2.25 (3H, s, H_3-21 of Ag), 1.69 (3H, d, J=6.5 Hz, H_3-6 of Rha), 1.07 (3H, s, H_3-19 of Ag), 0.94 (3H, s, H_3-18 of Ag). ^{13}C-NMR data: see Table 1.

3: Amorphous powder. $[\alpha]_D^{24}$ −56.6° (c=0.4, pyridine). IR (KBr) cm^{-1}: 3402 (OH), 1705 (ketone). Positive FAB-MS m/z: 809 $[M+Na]^+$. HR-positive FAB-MS m/z: 809.4077 $[M+Na]^+$ (Calcd for $C_{39}H_{62}O_{16}Na$: 809.3936). ^{1}H-NMR (in pyridine-d_5, 500 MHz) δ: 6.42 (1H, s, H-1 of Rha), 5.87 (1H, s, H-1 of Rha′), 5.34 (1H, br d, J=5.0 Hz, H-6 of Ag), 4.93 (1H, m, H-16 of Ag), *ca.* 4.90 (H-1 of Glc), 4.85 (1H, d, J=3.5 Hz, H-2 of Rha), 4.70 (1H, d, J=3.5 Hz, H-2 of Rha′), 4.64 (1H, dd, J=3.5, 9.5 Hz, H-3 of Rha), 4.56 (1H, dd, J=3.5, 9.5 Hz, H-3 of Rha′), 3.89 (1H, m, H-3 of Ag), 3.65 (1H, m, H-5 of Glc), 2.81 (1H, br dd, J=4.0, 12.0 Hz, Ha-4 of Ag), 2.74 (1H, br dd, J=12.0, 12.0 Hz, Hb-4 of Ag), 2.34 (3H, s, H_3-21 of Ag), 1.78 (3H, d, J=6.0 Hz, H_3-6 of Rha), 1.65 (3H, d, J=6.0 Hz, H_3-6 of Rha′), 1.45 (3H, s, H_3-18 of Ag), 1.06 (3H, s, H_3-19 of Ag). ^{13}C-NMR data: see Table 1.

4: Amorphous powder. $[\alpha]_D^{22}$ −39.8° (c=2.8, MeOH). IR (KBr) cm^{-1}: 3423 (OH), 1709 (ketone). Positive FAB-MS m/z: 1082 $[M+Na]^+$. HR-positive FAB-MS m/z: 1082.5308 $[M+Na]^+$ (Calcd for $C_{51}H_{81}NO_{22}Na$: 1082.5292). ^{1}H-NMR (in pyridine-d_5, 500 MHz) δ: 8.49 (1H, s, NH), 6.41 (1H, s, H-1 of Rha), 5.98 (1H, s, H-1 of Rha′), 5.69 (1H, ddd, J=5.0, 8.0, 8.0 Hz, H-16 of Ag), 5.31 (1H, br d, J=4.5 Hz, H-6 of Ag), 5.24 (1H, d, J=7.5 Hz, H-1 of Xyl), *ca.* 4.98 (H-1 of Glc), 4.84 (1H, d, J=3.5 Hz, H-2 of Rha), 4.67 (1H, d, J=3.5 Hz, H-2 of Rha′), 4.63 (1H, dd, J=3.5, 9.5 Hz, H-3 of Rha), 4.54 (1H, dd, J=3.5, 9.5 Hz, H-3 of Rha′), 3.89 (1H, m, H-3 of Ag), 3.75 (1H, br d like, J=9.5 Hz, H-5 of Glc), 3.42 (3H, s, OCH_3), 3.25 (1H, m, Ha-26 of Ag), 2.46 (1H, d, J=8.0 Hz, H-17 of Ag), 2.30 (3H, s, H_3-21 of Ag), 1.76 (3H, d, J=6.0 Hz, H_3-6 of Rha), 1.57 (3H, d, J=6.0 Hz, H_3-6 of Rha′), 1.40 (3H, s, H_3-18 of Ag), 1.04 (3H, s, H_3-19 of Ag), 0.76 (3H, d, J=6.5 Hz, H_3-27 of Ag). ^{13}C-NMR data: see Table 1.

5: Amorphous powder. $[\alpha]_D^{22}$ −72.2° (c=0.5, MeOH). IR (KBr) cm^{-1}: 3429 (OH). Positive FAB-MS m/z: 1085 $[M+Na]^+$. HR-positive FAB-MS m/z: 1085.5327 $[M+Na]^+$ (Calcd for $C_{51}H_{82}O_{23}Na$: 1085.5144). ^{1}H-NMR (in pyridine-d_5, 500 MHz) δ: 6.39 (1H, s, H-1 of Rha), 5.97 (1H, s, H-1 of Rha′), 5.51 (1H, s, H-26 of Ag), 5.34 (1H, d, J=8.0 Hz, H-1 of Glc′), 5.30 (1H, br d, J=3.5 Hz, H-6 of Ag), *ca.* 4.93 (H-1 of Glc), 4.83 (1H, br s, H-2 of Rha), 4.69 (1H, br s, H-2 of Rha′), 4.63 (1H, dd, J=3.0, 9.0 Hz, H-3 of Rha), 4.60 (1H, dd, J=6.5, 10.5 Hz, H-23 of Ag), 4.54 (1H, dd, J=3.0, 9.0 Hz, H-3 of Rha′), 3.87 (1H, m, H-3 of Ag), 3.66 (1H, m, H-5 of Glc), 2.80 (1H, br dd, J=3.5, 12.0 Hz, Ha-4 of Ag), 2.72 (1H, br dd, J=12.0, 12.0 Hz, Hb-4 of Ag), 2.47 (1H, dq, J=7.5, 7.5 Hz, H-25), 1.77 (3H, d, J=6.0 Hz, H_3-6 of Rha), 1.64 (3H, d, J=6.0 Hz, H_3-6 of Rha′), 1.27 (3H, d, J=6.5 Hz, H_3-21), 1.03 (3H, s, H_3-19 of Ag), 0.92 (3H, s, H_3-18 of Ag), 0.84 (3H, d, J=7.5 Hz, H_3-27 of Ag). ^{13}C-NMR data: see Table 1.

15: Amorphous powder. $[\alpha]_D^{31}$ −20.9° (c=1.9, pyridine). Negative FAB-MS m/z: 293 $[M-H]^-$. ^{1}H-NMR (in pyridine-d_5, 500 MHz) δ: 4.83 (1H, d, J=8.0 Hz, H-1 of Glc), 4.57 (1H, dd, J=2.0, 11.5 Hz, Ha-6 of Glc), 4.41 (1H, dd, J=5.0, 11.5 Hz, Hb-6 of Glc), *ca.* 4.26 (2H, H-3 of Glc and H-4 of Glc), 4.04 (1H, dd, J=8.0, 8.5 Hz, H-2 of Glc), *ca.* 3.96 (2H, H-5 of Glc and Ha-5 of Ag), 3.55 (1H, dd, J=6.0, 9.5 Hz, Hb-5 of Ag), *ca.* 2.56 (2H, H_2-2 of Ag), 2.07 (1H, m), 1.78 (1H, m), 1.69 (1H, m), 0.96 (3H, d, J=6.5 Hz, H_3-6 of Ag). ^{13}C-NMR (in pyridine-d_5, 125 MHz) δ: 176.2 (C-1 of Ag), 104.9 (C-1 of Glc), 78.6 (C-3 of Glc or C-5 of Glc), 78.5 (C-3 of Glc or C-5 of Glc), 75.2 (C-2 of Glc), 74.9 (C-5 of Ag), 71.7 (C-4 of Glc), 62.9 (C-6 of Glc), 33.6 (C-4 of Ag), 32.6 (C-2 of Ag), 29.6 (C-3 of Ag), 17.1 (C-6 of Ag).

16: Amorphous powder. $[\alpha]_D^{31}$ −17.0° (c=0.4, pyridine). ^{1}H-NMR (in pyridine-d_5, 500 MHz) δ: 4.81 (1H, d, J=8.0 Hz, H-1 of Glc), 4.58 (1H, dd, J=2.5, 11.5 Hz, Ha-6 of Glc), 4.41 (1H, dd, J=5.5, 11.5 Hz, Hb-6 of Glc), *ca.* 4.26 (2H, H-3 of Glc and H-4 of Glc), 4.04 (1H, dd, J=8.0, 8.5 Hz, H-2 of Glc), 3.96 (1H, m, H-5 of Glc), 3.91 (1H, dd, J=6.0, 9.0 Hz, Ha-5 of Ag), 3.58 (3H, s, OCH_3), 3.49 (1H, dd, J=6.0, 9.0 Hz, Hb-5 of Ag), *ca.* 2.37 (2H, H_2-2 of Ag), 1.91 (1H, m), 1.84 (1H, m), 1.53 (1H, m), 0.89 (3H, d, J=6.5 Hz, H_3-6 of Ag).

Sugar Analysis Compounds **1**—**5** (3—5 mg) were each heated in 2 M HCl–dioxane (2 : 1, 1.5 ml) at a temperature of 95°C for 1 h. The reaction mixture was extracted with AcOEt. The aqueous layer was neutralized with Amberlite MB-3 (Organo Co.) and then evaporated under reduced pressure to give a monosaccharide fr. This fr. was analyzed by HPLC under the following conditions: column, Shodex RS-Pac DC-613, Showa Denko, 150 mm×6.0 mm; solvent, CH_3CN–H_2O (3 : 1); flow rate, 1.0 ml/min; column temperature, 70 °C; detector, JASCO OR-2090 plus; pump, JASCO PU-2080; and column oven, JASCO CO-2060. The retention time (t_R) and optical activity of each of the monosaccharides were detected as follows. L-Rhamnose [t_R (min) 4.2; optical activity, negative], D-xylose [t_R (min) 5.1; optical activity, positive], and D-glucose [t_R (min) 6.8; optical activity, positive] for **1**; L-rhamnose [t_R (min) 4.2; optical activity, negative], D-glucose [t_R (min) 6.8; optical activity, positive], and D-galactose [t_R (min) 7.4; optical activity, positive] for **2**; L-rhamnose [t_R (min) 4.2; optical activity, negative] and D-glucose [t_R (min) 6.9; optical activity, positive] for **3**; L-rhamnose [t_R (min) 4.1; optical activity, negative], D-xylose [t_R (min) 5.1; optical activity, positive], and D-glucose [t_R (min) 6.8; optical activity, positive] for **4**; L-rhamnose [t_R (min) 4.1; optical activity, negative] and D-glucose [t_R (min) 6.8; optical activity, positive] for **5**.

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