Two New Nortriterpenoid Glycosides and a New Phenylpropanoid Glycoside from the Bulbs of *Scilla scilloides*

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Two new norlanostane-type triterpenoid glycosides and a new phenylpropanoid glycoside were isolated from the bulbs of *Scilla scilloides* Druce (Liliaceae), along with two known alkaloids. Their chemical structures were determined on the basis of spectroscopic data as well as chemical evidence.

Key words *Scilla scilloides*; triterpenoid; phenylpropanoid; glycoside; alkaloid; Liliaceae

Scilla scilloides Druce is a perennial herb belonging to the Liliaceae family. The bulb of this plant is consumed and has been used as a traditional medicine to promote blood circulation, as an antiinflammatory agent and as an analgesic.[1)] With regard to the chemical constituents of this bulb, the presence of homoisoflavones and norlanostane- and lanostane-type triterpenoids has been previously reported.[2–6)] In preceding papers,[7,8)] we reported the isolation and structural elucidation of a new homostilbene, two new homoisoflavones, three new norlanostane-type triterpenoid glycosides, and two new lanostane-type triterpenoid glycosides from the methanol (MeOH) extract of fresh bulbs of *S. scilloides* along with 14 known compounds including a homostilbene, seven homoisoflavones, a xanthone, a lignan, three norlanostane-type triterpenoids, and a norlanostane-type triterpenoid glycoside. As part of an ongoing study of this plant, the isolation and structural characterization of two new norlanostane-type triterpenoid glycosides and a new phenylpropanoid glycoside along with two known alkaloids from the MeOH extract are reported herein.

The MeOH extract of fresh bulbs of *S. scilloides* was suspended in H_2O and successively extracted with ethyl acetate (EtOAc) and *n*-butanol (BuOH). Repeated chromatography of the aqueous layer with Diaion HP20, Sephadex LH-20, Chromatorex octadecyl silica (ODS), and silica gel column chromatography, as well as HPLC on ODS led to the isolation of five compounds (**1**–**5**).

Compounds **4** and **5** were identified as narciclasine[9)] and *O*-methyllycorenine,[10)] respectively, based on their physical and spectral data, although ^{1}H- and ^{13}C-NMR spectral data in pyridine-d_5 of **4** have not been reported in the literature (Fig. 1).

Compound **1**, tentatively named scillanostaside F, was obtained as an amorphous powder. In negative-ion FAB-MS, **1** gave a $[M-H]^-$ ion peak at *m/z* 1397 along with fragment ion peaks at *m/z* 1251 [1397−146 ($C_6H_{10}O_4$, 6-deoxyhexosyl unit)]$^-$, 1235 [1397−162 ($C_6H_{10}O_5$, hexosyl unit)]$^-$, 1089 [1235−146]$^-$, 1073 [1235−162]$^-$, 927 [1073−146]$^-$, 765 [927−162]$^-$, 633 [765−132 ($C_5H_8O_4$, pentosyl unit)]$^-$, and 471 [633−162]$^-$ (Fig. 2). High-resolution (HR)-positive-ion FAB-MS showed the molecular formula of **1** to be $C_{64}H_{102}O_{33}$. The ^{1}H-NMR spectrum of **1** indicated signals due to four tertiary methyl groups [δ 1.67 (s), 1.49 (s), 1.14 (s), 0.88 (s)], two secondary methyl groups [δ 1.74 (d, J=6.5 Hz), 1.04 (d, J=6.5 Hz)], one primary methyl group [δ 1.06 (t, J=7.0 Hz)], and six anomeric protons [δ 6.23 (s), 5.30 (d, J=3.5 Hz), 5.19 (d, J=7.5 Hz), 5.10 (d, J=8.0 Hz), 4.99 (d, J=7.5 Hz), 4.92 (d, J=8.0 Hz)]. The ^{13}C-NMR spectrum of **1** exhibited signals due

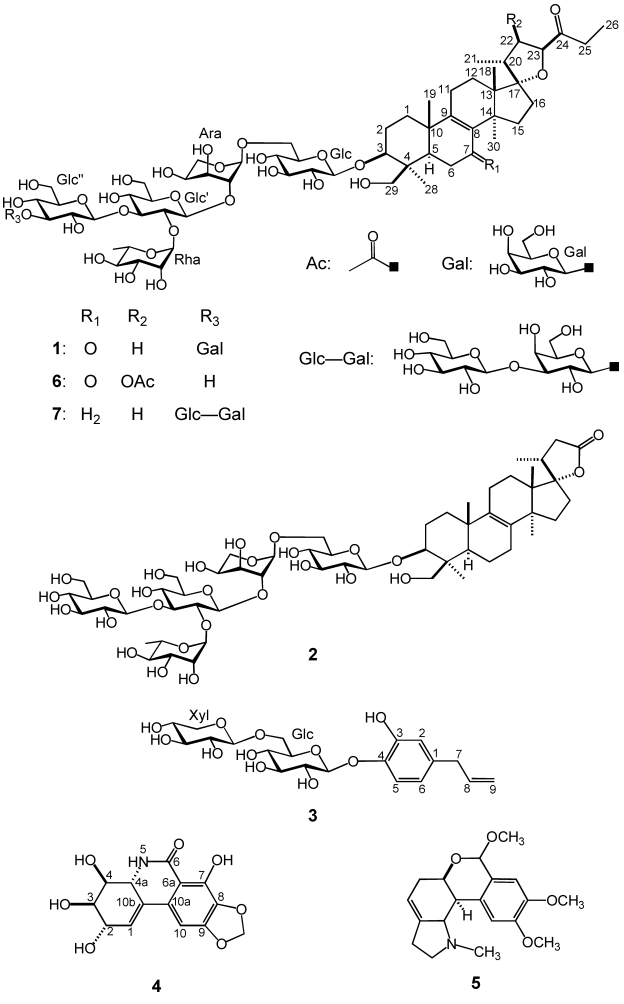

Fig. 1. Structures of **1**—**5**

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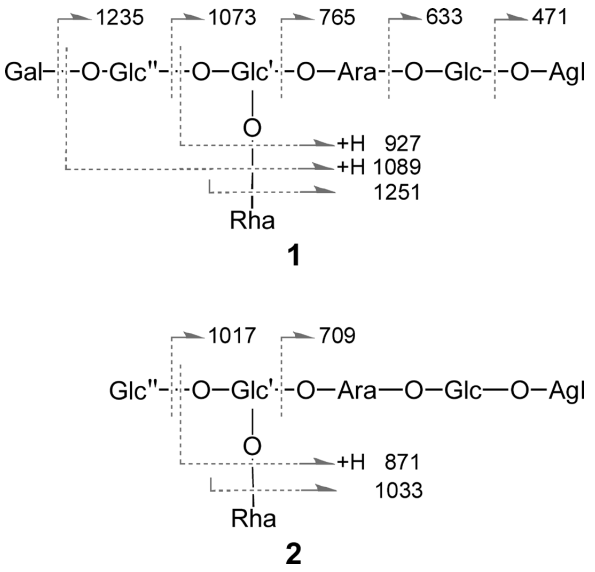

Fig. 2. Fragment Ions Observed in the Negative-Ion FAB-MS of **1** and **2**

to two keto carbonyl carbons (δ 212.4, 198.1), two olefinic carbons (δ 164.3, 139.5), and six anomeric carbons (δ 106.0, 105.7, 103.7, 102.2, 101.8, 101.1). The ^{1}H- and ^{13}C-NMR spectra were similar to those of scillanostaside B (**6**),[8] apart from the loss of signals due to an acetoxy group and an oxygenated methine group and the appearance of signals due to an additional methylene group and an additional hexosyl unit. A detailed analysis of these NMR spectral signals was performed using the ^{1}H–^{1}H correlation spectroscopy (COSY), heteronuclear multiple-quantum coherence (HMQC), heteronuclear multiple-bond correlation (HMBC), and total correlation spectroscopy (TOCSY) techniques. In the HMBC spectrum of **1**, the keto carbonyl carbon at δ 198.1 showed long-range correlations with the methylene protons assignable to H_2-6 of an aglycone moiety (Agl) at δ *ca.* 2.79 and *ca.* 2.76, with which the methine proton due to H-5 of Agl at δ 1.88 exhibited correlations in the ^{1}H–^{1}H COSY spectrum. Further, a cross-peak between the keto carbonyl carbon at δ 212.4 and the methyl protons due to H_3-26 of Agl at δ 1.06 was observed in the HMBC spectrum. Thus, the planar structure of **1** was a hexaglycoside of 17,23-epoxy-3,28-dihydroxy-27-nor-lanost-8-ene-7,24-dione, as illustrated in Fig. 3.

On acidic hydrolysis, **1** afforded L-rhamnose, L-arabinose, D-glucose, and D-galactose, which were identified by optical rotation using chiral detection in HPLC analysis, together with several unidentified artificial aglycones. The coupling constants of the signals due to the anomeric protons in the ^{1}H-NMR spectrum and the chemical shifts[11–13] of the signals due to arabinosyl and rhamnosyl units in the ^{13}C-NMR spectrum suggested that all monosaccharide units were of the pyranose form, and further, that the mode of glycosidic linkages of the glucopyranosyl and galactopyranoyl units were β in $^4C_1$ conformation and those of the arabinopyranosyl and rhamnopyranosyl units were α in $^1C_4$ conformation. The HMBC spectrum of **1** showed key correlations between H-1 of the first glucosyl unit (Glc) and C-3 of the Agl, H-1 of the second glucosyl unit (Glc′) and C-2 of the arabinosyl unit (Ara), H-1 of the third glucosyl unit (Glc″) and C-3 of Glc′, and H-1 of the galactosyl unit (Gal) and C-3 of Glc″ (Fig. 3). From these data, **1** was assumed to be a derivative of **6**, in which an acetoxy group at C-23 of Agl of **6** was cleaved and a β-D-galactopyranosyl unit was attached to OH-3 of Glc". This was confirmed by the following evidence. Comparison of the chemical shifts of ^{13}C-NMR signals due to the sugar

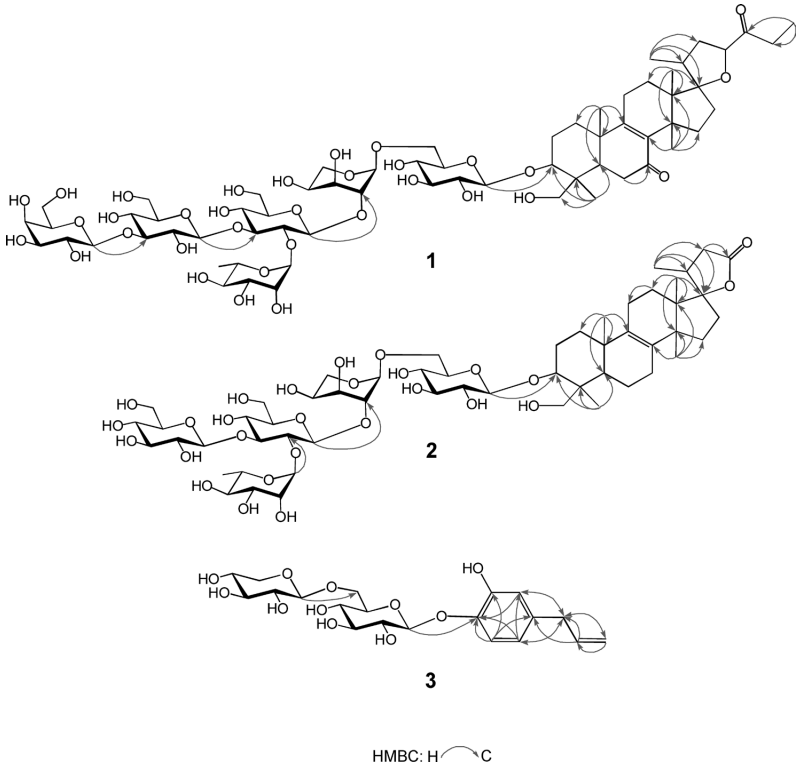

Fig. 3. ^{1}H–^{13}C Long-Range Correlations Observed in the HMBC Spectra of **1**–**3** (in Pyridine-d_5, 500 MHz)

moieties between **1** and **6** revealed glycosylation shifts[14,15] of −1.5, +9.8, and −1.9 ppm at C-2, C-3, and C-4 of Glc″, respectively, with the appearance of signals due to one terminal *β*-D-galactopyranosyl unit,[11] while the other signals due to the sugar moiety, including deshielded signals, which are subject to glycosylation shift, assignable to C-6 of Glc and C-2 of Glc′ and signals corresponding to a terminal *α*-L-rhamnopyranosyl unit,[11,14,15] were almost same as those of **6**. In addition, the fragment ion peaks at *m/z* 765 and 633 in the negative-ion FAB-MS of **1** suggested that Ara should be attached to Glc (Fig. 2). The stereochemistry of Agl was defined on the basis of the nuclear Overhauser effect spectroscopy (NOESY) and ^{13}C-NMR spectra of **1**. In the NOESY spectrum, key nuclear Overhauser effect (NOE) correlations were observed between H-3 of Agl and H_3-28 of Agl, H-5 of Agl and H_3-28 of Agl, H_3-18 of Agl and H-20 of Agl, and H_3-19 of Agl and Ha,b-29 of Agl (Fig. 4). Moreover, the ^{13}C-NMR spectral data of C-1–C-13, C-18, and C-19 of Agl in **1** were superimposable on those of **6**; in contrast, the data of C-20–C-26 of Agl were quite similar to those of scillascilloside G-1 (**7**),[5] but the data of C-20, C-21, C-23, and C-24 were not imposable on those of (23*R*)-17*α*,23-epoxy-3*β*,29-dihydroxy-27-nor-lanost-8-ene-24-one glycosides.[16] The structure of **1** was thus concluded to be (23*S*)-17*α*,23-epoxy-3*β*,29-dihydroxy-27-nor-lanost-8-ene-7,24-dione 3-*O*-*α*-L-rhamnopyranosyl-(1→2)-[*O*-*β*-D-galactopyranosyl-(1→3)-*O*-*β*-D-glucopyranosyl-(1→3)]-*O*-*β*-D-glucopyranosyl-(1→2)-*O*-*α*-L-arabinopyranosyl-(1→6)-*β*-D-glucopyranoside.

Compound **2**, tentatively named scillanostaside G, was obtained as an amorphous powder, and its negative-ion FAB-MS showed a $[M-H]^-$ ion peak at *m/z* 1179 together with fragment ion peaks at *m/z* 1033 $[1179-146]^-$, 1017 $[1179-162]^-$, 871 $[1017-146]^-$, and 709 $[871-162]^-$ (Fig. 2). The molecular formula of **2** was determined to be $C_{55}H_{88}O_{27}$ using HR-negative-ion FAB-MS. The ^{1}H-NMR spectrum of **2** showed signals due to four tertiary methyl groups [*δ* 1.57 (s), 1.20 (s), 0.91 (s), 0.86 (s)], two secondary methyl groups [*δ* 1.76 (d, *J*=6.5 Hz), 1.01 (d, *J*=7.0 Hz)], and five anomeric protons [*δ* 6.34 (d, *J*=1.0 Hz), 5.32 (d, *J*=2.5 Hz), 5.19 (d, *J*=8.0 Hz), 5.03 (d, *J*=8.0 Hz), 4.97 (d, *J*=8.0 Hz)]. The ^{13}C-NMR spectrum of **2** indicated signals due to a carboxyl carbon (*δ* 176.8), two olefinic carbons (*δ* 135.2, 134.6), and five anomeric carbons (*δ* 106.0, 104.3, 102.5, 102.0, 101.1). These NMR spectral signals were assigned in detail with the aid of 2D-NMR techniques as done for **1**, and the planar structure of **2** was elucidated as shown in Fig. 3. In addition, the ^{13}C-NMR spectral data of the sugar moiety of **2** were considerably similar to those of **6**. From the foregoing data, it was proposed that the aglycone of **2** was 24,25,26-trinor-23-oxo-15-deoxyeucosterol (also known as SSG-4),[4] which was previously isolated from the bulbs of *S. scilloides*, and the sugar moiety was the same as that of **6**. These inferences were confirmed by the generation of L-rhamnose, L-arabinose, and D-glucose upon acidic hydrolysis of **2**, and from the NOE correlations observed between H-3 of Agl and H_3-28 of Agl, H-5 of Agl and H_3-28 of Agl, H_3-19 of Agl and Ha-29 of Agl, and H_3-18 of Agl and H-20 of Agl in the NOESY spectrum of **2** (Fig. 4). Consequently, the structure of **2** was concluded to be 24,25,26-trinor-23-oxo-15-deoxyeucosterol 3-*O*-*α*-L-rhamnopyranosyl-(1→2)-[*O*-*β*-D-glucopyranosyl-(1→3)]-*O*-*β*-D-glucopyranosyl-(1→2)-*O*-*α*-L-arabinopyranosyl-(1→6)-*β*-D-glucopyranoside.

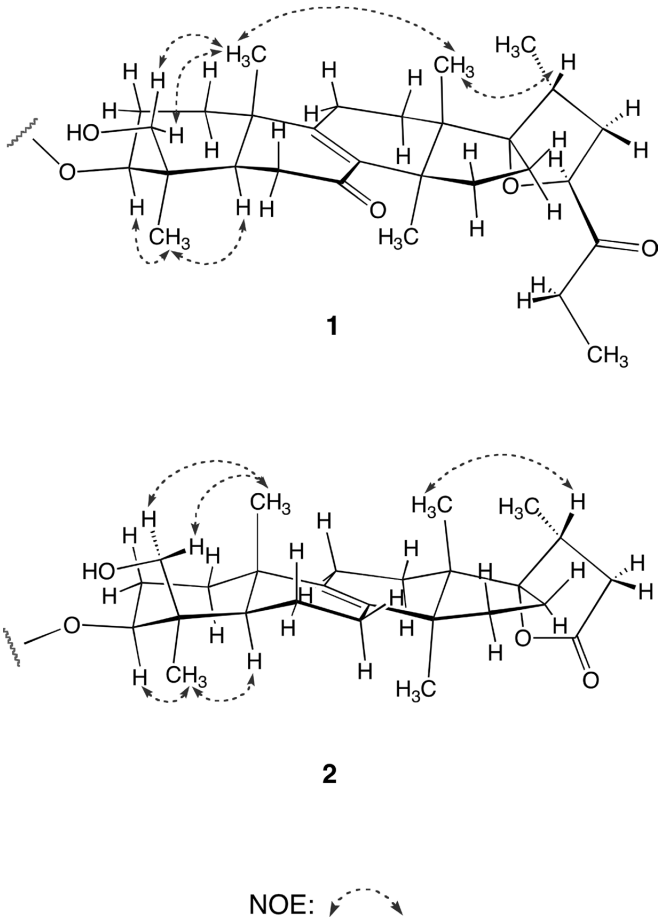

Fig. 4. Key NOE Correlations Observed in the NOESY Spectra of **1** and **2** (in Pyridine-d_5, 500 MHz)

Compound **3** was obtained as an amorphous powder. In positive-ion FAB-MS, **3** gave $[M+Na]^+$ and $[M+H]^+$ ion peaks at *m/z* 467 and 445, respectively. HR-positive-ion FAB-MS showed the molecular formula of **3** to be $C_{20}H_{28}O_{11}$. The ^{1}H-NMR spectrum of **3** indicated signals due to three aromatic protons for an ABX pattern [*δ* 7.13 (d, *J*=8.5 Hz), 6.68 (d, *J*=2.0 Hz), 6.63 (dd, *J*=2.0, 8.5 Hz)], a vinyl group [*δ* 5.92 (ddt, *J*=10.5, 17.0, 7.0 Hz), 5.04 (ddt, *J*=2.0, 17.0, 2.0 Hz), 5.01 (ddt, *J*=2.0, 10.5, 2.0 Hz)], and two anomeric protons [*δ* 4.71 (d, *J*=7.5 Hz), 4.33 (d, *J*=7.5 Hz)]. The ^{13}C-NMR spectrum of **3** exhibited signals due to eight olefinic carbons (*δ* 148.7, 145.3, 139.2, 137.4, 121.4, 119.4, 117.5, 116.0), two anomeric carbons (*δ* 105.6, 104.7), and one methylene carbon (*δ* 40.8). On acidic hydrolysis, **3** afforded D-xylose and D-glucose. A detailed analysis of these NMR spectral signals suggested that **3** is a diglycoside of demethyleugenol. Further, key correlations were observed between H-1 of glucosyl unit (Glc) and C-4 of Agl and H-1 of xylosyl unit (Xyl) and C-6 of Glc in the HMBC spectrum, as illustrated in Fig. 3. In addition, when compared with the ^{13}C-NMR spectral data of methyl *β*-D-glucopyranoside from the literature,[11] glycosylation shifts[14,15] in the data of **3** were observed at C-5 (−0.6 ppm) and C-6 (+7.5 ppm) of Glc. The structure of **3** was thus concluded to be demethyleugenol 4-*O*-*β*-D-xylopyranosyl-(1→6)-*O*-*β*-D-glucopyranoside.

To the best of our knowledge, **1**, **2**, and **3** are new compounds, and the isolation of **4** and **5** from *S. scilloides* are described here for the first time. Among them, **1** has a new

Table 1. ^{1}H-NMR Spectral Data for Aglycone Moiety of **1** and **2** (in Pyridine-d_5, 500 MHz)

	1	2
1a	*ca.* 1.78	*ca.* 1.65
1b	1.35 ddd (3.0, 13.5, 13.5)	1.13 m
2a	2.34 m	*ca.* 2.27
2b	*ca.* 2.05	*ca.* 2.01
3	*ca.* 3.60	3.59 dd (5.2, 12.0)
5	1.88 dd (7.0, 10.5)	*ca.* 1.27
6a	*ca.* 2.79	*ca.* 1.81
6b	*ca.* 2.76	1.51 m
7a		*ca.* 2.07
7b		*ca.* 1.90
11a	*ca.* 2.47	*ca.* 2.07
11b	*ca.* 2.20	*ca.* 1.93
12a	*ca.* 2.47	*ca.* 2.23
12b	1.55 m	1.43 m
15a	2.64 br dd (10.5, 10.5)	*ca.* 1.65
15b	*ca.* 2.03	*ca.* 1.31
16a	*ca.* 2.23	*ca.* 2.25
16b	*ca.* 1.67	*ca.* 2.02
18	0.88 s	0.86 s
19	1.14 s	0.91 s
20	*ca.* 2.05	2.32 dq (7.0, 7.0)
21	1.04 d (6.5)	1.01 d (7.0)
22a	2.02 m	2.77 dd (7.0, 16.5)
22b	*ca.* 1.76	2.05 d (16.5)
23	*ca.* 4.66	
25a	*ca.* 2.57	
25b	*ca.* 2.58	
26	1.06 dd (7.0, 7.0)	
28	1.49 s	1.57 s
29a	4.41 d (11.0)	4.42 d (11.5)
29b	3.82 br d (11.0)	*ca.* 3.65
30	1.67 s	1.20 s

δ in ppm from tetramethylsilane (TMS) (coupling constants (J) in Hz are given in parentheses).

Table 2. ^{1}H-NMR Spectral Data for Sugar Moiety of **1** and **2** (in Pyridine-d_5, 500 MHz)

	1	2
Glc-1	4.92 d (7.5)	4.97 d (8.0)
2	*ca.* 3.96	3.98 dd (8.0, 9.0)
3	*ca.* 4.15	*ca.* 4.16
4	*ca.* 4.14	*ca.* 4.16
5	3.99 m	*ca.* 4.01
6a	4.56 dd (3.5, 11.0)	*ca.* 4.54
6b	*ca.* 4.25	*ca.* 4.25
Ara-1	5.30 d (3.5)	5.32 d (2.5)
2	*ca.* 4.67	*ca.* 4.67
3	*ca.* 4.65	*ca.* 4.67
4	*ca.* 4.52	*ca.* 4.55
5	*ca.* 4.36	4.38 dd (7.5, 11.5)
5	*ca.* 3.91	3.92 dd (3.0, 11.5)
Glc′-1	5.19 d (7.5)	5.19 d (8.0)
2	*ca.* 4.18	*ca.* 4.20
3	*ca.* 4.06	*ca.* 4.07
4	*ca.* 4.06	*ca.* 4.09
5	*ca.* 3.61	*ca.* 3.64
6	*ca.* 4.22	*ca.* 4.25
6	*ca.* 4.14	*ca.* 4.14
Rha-1	6.23 s	6.34 d (1.0)
2	4.82 br d (3.0)	4.83 dd (1.0, 3.0)
3	4.62 dd (3.0, 9.5)	4.63 dd (3.0, 9.5)
4	4.26 dd (9.5, 9.5)	4.28 dd (9.5, 9.5)
5	4.88 dq (9.5, 6.5)	4.88 dq (9.5, 6.5)
6	1.74 d (6.5)	1.76 d (6.5)
Glc″-1	4.99 d (7.5)	5.03 d (8.0)
2	*ca.* 3.95	*ca.* 3.98
3	*ca.* 4.14	*ca.* 4.20
4	*ca.* 3.92	*ca.* 4.09
5	*ca.* 3.92	*ca.* 3.98
6	4.43 dd (2.5, 11.0)	*ca.* 4.53
6	*ca.* 4.10	*ca.* 4.25
Gal-1	5.10 d (8.0)	
2	4.51 dd (8.0, 8.5)	
3	*ca.* 4.12	
4	4.46 d (3.5)	
5	*ca.* 4.10	
6a	4.34 dd (5.0, 10.0)	
6b	*ca.* 4.08	

δ in ppm from TMS (coupling constants (J) in Hz are given in parentheses). Glc, glucopyranosyl; Ara, arabinopyranosyl; Rha, rhamnopyranosyl; Gal, galactopyranosyl.

aglycone and **2** is the first example of a glycoside of SSG-4; furthermore, the sugar moiety attached to C-3 of the aglycone of **1** is a new hexasaccharide.

Experimental

All instruments and materials used were the same as cited in a previous report[17] unless otherwise specified.

Plant Material The bulbs of *S. scilloides* were cultivated in Kumamoto prefecture, Japan, and were harvested in August 2005, and identified by one of authors (T. Nohara). A voucher specimen (SCK2005) has been deposited at the laboratory of Natural Products Chemistry, School of Agriculture, Tokai University.

Extraction and Isolation The crushed fresh bulbs of *S. scilloides* (18.5 kg) were extracted with MeOH at room temperature, and the solvent was removed under reduced pressure to give a syrup (3521.7 g). The MeOH extract was suspended in H_2O and successively extracted with EtOAc and BuOH. The aqueous layer was chromatographed over Diaion HP20 column (Mitsubishi Chemical Industries Co., Ltd., Tokyo, Japan), eluted with H_2O, MeOH, and acetone. The MeOH eluate (76.7 g) was further subjected to Diaion HP20 column chromatography using gradient mixtures of H_2O–MeOH (50% MeOH, 60% MeOH, 70% MeOH, 80% MeOH, 90% MeOH, 100% MeOH) as eluents to give fractions (frs.) 1–4. Fraction (fr.) 1 (14.55 g) was chromatographed over Sephadex LH-20 column (Pharmacia Fine Chemicals, Uppsala, Sweden) using gradient mixtures of H_2O–MeOH (50% MeOH, 100% MeOH) as eluents to give frs. 1.1–1.6. HPLC [Nacalai Tesque, Inc., Kyoto, Japan, Cosmosil 5C18 AR-II, 20 mm i.d.×250 mm (column 1)] of fr. 1.4 (3.265 g) with 40% MeOH as eluent afforded **3** (38 mg). Fraction 1.5 (566 mg) was subjected to Chromatorex ODS column (Fuji Silysia Chemical, Ltd., Aichi, Japan) chromatography using gradient mixtures of H_2O–MeOH (20% MeOH, 30% MeOH, 40% MeOH, 50% MeOH, 60% MeOH, 100% MeOH) as eluents to afford frs. 1.5.1–1.5.4. HPLC (column 1) of fr. 1.5.2 (193 mg) with 20%

Table 3. ^{13}C-NMR Spectral Data for **1** and **2** (in Pyridine-d_5, 125 MHz)

	1	**2**		**1**	**2**
Agl-1	34.8	35.6	Glc-1	106.0	106.0
2	27.2	27.4	2	75.2	75.4
3	87.6	88.9	3	78.0	78.5
4	43.9	44.4	4	72.6	72.6
5	50.7	51.7	5	75.6	75.6
6	37.3	18.7	6	68.5	68.6
7	198.1	26.7	Ara-1	101.1	101.1
8	139.5	135.2	2	77.5	77.7
9	164.3	134.6	3	71.5	71.7
10	39.5	36.8	4	66.7	66.8
11	23.4	20.8	5	62.7	62.8
12	24.6	24.7	Glc′-1	102.2	102.5
13	49.0	48.9	2	76.5	76.9
14	49.5	50.8	3	89.1	89.1
15	33.5	31.6	4	69.0	69.1
16	40.1	39.1	5	77.4	77.8
17	95.6	97.9	6	61.6	61.8
18	19.2	17.9	Rha-1	101.8	102.0
19	18.0	19.5	2	71.9	72.2
20	43.6	41.7	3	72.4	72.6
21	17.1	17.6	4	73.9	74.1
22	36.7	39.1	5	69.5	69.8
23	81.5	176.8	6	18.6	18.7
24	212.4		Glc″-1	103.7	104.3
25	32.1		2	73.4	75.0
26	7.5		3	88.2	78.2
28	22.4	23.1	4	69.5	71.4
29	62.7	63.1	5	77.8	78.6
30	27.2	25.7	6	61.9	62.3
			Gal-1	105.7	
			2	72.3	
			3	74.8	
			4	69.9	
			5	77.1	
			6	61.9	

δ in ppm from TMS. Agl, aglycone moiety; Glc, glucopyranosyl; Ara, arabinopyranosyl; Rha, rhamnopyranosyl; Gal, galactopyranosyl.

MeOH as eluent furnished **4** (12 mg). Fraction 2 (31.4 g) was chromatographed over silica gel column (Merck, Art. 1.09385; Merck, Darmstadt, Germany) using gradient mixtures of $CHCl_3$–MeOH–H_2O (8 : 2 : 0.2, 7 : 3 : 0.5, 6 : 4 : 1, 0 : 1 : 0) as eluents to give frs. 2.1–2.6. Fraction 2.1 (1.387 g) was subjected to silica gel column chromatography using gradient mixtures of hexane–acetone (10 : 1, 9 : 1, 8 : 1, 5 : 1, 3 : 1, 2 : 1, 1 : 1, 1 : 0) as eluents to afford frs. 2.1.1–2.1.8. Fraction 2.1.5 (171 mg) was subjected to HPLC (column 1) with 60% MeOH as eluent to give **5** (19 mg). Fraction 2.3 (7.69 g) was subjected to Chromatorex ODS column chromatography using gradient mixtures of H_2O–MeOH (60% MeOH, 70% MeOH, 80% MeOH, 90% MeOH, 100% MeOH) as eluents to afford frs. 2.3.1–2.3.6. HPLC (column 1) of fr. 2.3.5 (1.997 g) with 60% MeOH as eluent furnished **1** (58 mg) and **2** (38 mg).

1: Amorphous powder. $[\alpha]_D^{25}$ −39.6° (c=1.6, pyridine). UV λ_{max} (MeOH) nm (logε): 253 (3.75). Positive-ion FAB-MS m/z: 1421 $[M+Na]^+$. HR-positive-ion FAB-MS m/z: 1421.6187 (Calcd for $C_{64}H_{102}O_{33}Na$: 1421.6202). Negative-ion FAB-MS m/z: 1397 $[M-H]^-$, 1251 $[1397-146]^-$, 1235 $[1397-162]^-$, 1089 $[1235-146]^-$, 1073 $[1235-162]^-$, 927 $[1073-146]^-$, 765 $[927-162]^-$, 633 $[765-132]^-$, 471 $[633-162]^-$. ^{1}H-NMR spectral data: see Tables 1 and 2. ^{13}C-NMR spectral data: see Table 3.

2: Amorphous powder. $[\alpha]_D^{25}$ −14.3° (c=1.1, pyridine). Negative-ion FAB-MS m/z: 1179 $[M-H]^-$, 1033 $[1179-146]^-$, 1017 $[1179-162]^-$, 871 $[1017-146]^-$, 709 $[871-162]$. HR-negative-ion FAB-MS m/z: 1179.5468 (Calcd for $C_{55}H_{87}O_{27}$: 1179.5435). ^{1}H-NMR spectral data: see Tables 1 and 2. ^{13}C-NMR spectral data: see Table 3.

3: Amorphous powder. $[\alpha]_D^{16}$ −64.8° (c=4.2, MeOH). UV λ_{max} (MeOH) nm (logε): 276 (3.31). Positive-ion FAB-MS m/z: 467 $[M+Na]^+$, 445 $[M+H]^+$. HR-positive-ion FAB-MS m/z: 445.1710 (Calcd for $C_{20}H_{29}O_{11}$: 445.1710). ^{1}H- and ^{13}C-NMR spectral data: see Table 4.

4: Amorphous powder. $[\alpha]_D^{16}$ +102.0° (c=1.5, pyridine). UV λ_{max} (MeOH) nm (logε): 251 (3.93). Positive-ion FAB-MS m/z: 308 $[M+H]^+$. HR-positive-ion FAB-MS m/z: 308.0768 (Calcd for $C_{14}H_{14}O_7N$: 308.0770). ^{1}H-NMR spectral data (in pyridine-d_5, 500 MHz) δ: 14.24 (1H, s, OH-7), 9.53 (1H, s, H-5), 6.89 (1H, s, H-10), 6.66 (1H, dd, J=2.5, 3.5 Hz, H-1), 6.05 (1H, d, J=1.0 Hz, OCH_2O), 6.04 (1H, d, J=1.0 Hz, OCH_2O), 5.14 (1H, brd, J=8.5 Hz, H-4a), 5.01 (1H, m, H-2), 4.80 (1H, brs, H-3), 4.78 (1H, dd, J=2.5, 8.5 Hz, H-4). ^{13}C-NMR spectral

Table 4. ^{1}H- and ^{13}C-NMR Spectral Data for **3** (in Pyridine-d_5)

	δ_H	δ_C
Agl-1		137.4
2	6.68 d (2.0)	117.5
3		148.7
4		145.3
5	7.13 d (8.5)	119.4
6	6.63 dd (2.0, 8.5)	121.4
7	3.26 br d like (7.0)	40.8
8	5.92 ddt (10.5, 17.0, 7.0)	139.2
9a	5.04 ddt (2.0, 17.0, 2.0)	116.0
9b	5.01 ddt (2.0, 10.5, 2.0)	
Glc-1	4.71 d (7.5)	104.7
2	3.49 dd (7.5, 9.0)	75.0
3	3.46 dd (9.0, 9.0)	77.6
4	3.41 dd (9.0, 9.0)	71.6
5	3.60 ddd (2.0, 6.5, 9.0)	77.5
6a	4.12 dd (2.0, 11.5)	70.0
6b	3.78 dd (6.5, 11.5)	
Xyl-1	4.33 d (7.5)	105.6
2	3.23 dd (7.5, 9.5)	75.2
3	3.32 dd (9.5, 9.5)	77.8
4	3.50 ddd (6.0, 9.5, 10.5)	71.4
5a	3.86 dd (6.0, 11.5)	67.1
5b	3.17 dd (10.5, 11.5)	

δ in ppm from TMS (coupling constants (J) in Hz are given in parentheses). ^{1}H, 500 MHz; ^{13}C, 125 MHz. Agl, aglycone moiety: Glc, glucopyranosyl; Xyl, xylopyranosyl.

data (in pyridine-d_5, 125 MHz) δ: 170.2 (C-6), 153.0 (C-9), 146.6 (C-7), 134.5 (C-8), 132.9 (C-10a), 131.1 (C-10b), 125.1 (C-1), 107.0 (C-6a), 102.5 (OCH_2O), 96.1 (C-10), 74.6 (C-3), 71.0 (C-2), 70.9 (C-4), 54.0 (C-4a). The ^{1}H-NMR spectral data in DMSO-d_6 (500 MHz) were superimposable on those in the literature.[9]

Sugar Analysis Compounds **1** (5 mg), **2** (5 mg), and **3** (5 mg) were each heated in 2 M HCl (1 mL) at a temperature of 95° for 2 h. The reaction mixture was extracted with EtOAc (1 mL). The aqueous layer was neutralized with Amberlite MB-3 column (Organo Co., Tokyo, Japan, 13 mm i.d.×230 mm) 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, Tokyo, Japan, 6.0 mm i.d.×150 mm; solvent, CH_3CN–H_2O (4 : 1 or 3 : 1); flow rate, 1.0 mL/min; column temperature, 70°C; detector, JASCO OR-2090 plus (JASCO Co., Tokyo, Japan); 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, 4.8 min; optical activity, negative], L-arabinose [t_R, 7.8 min; optical activity, positive], D-glucose [t_R, 10.8 min; optical activity, positive], and D-galactose [t_R, 11.3 min; optical activity, positive] for **1** [solvent, CH_3CN–H_2O (4 : 1)]; L-rhamnose [t_R, 4.7 min; optical activity, negative], L-arabinose [t_R, 7.7 min; optical activity, positive], and D-glucose [t_R, 10.8 min; optical activity, positive] for **2** [solvent, CH_3CN–H_2O (4 : 1); D-xylose [t_R, 5.1 min; optical activity, positive] and D-glucose [t_R, 6.8 min; optical activity, positive] for **3** [solvent, CH_3CN–H_2O (3 : 1)]. However, the EtOAc extract exhibited several spots by TLC, and the aglycones of **1** and **2** could not be obtained.

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