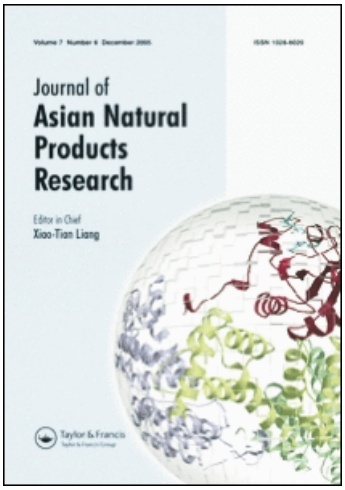

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ORIGINAL ARTICLE

Three new secoiridoid glycoside dimers from *Swertia mileensis*

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Three new secoiridoid glycoside dimers named swerilactosides A–C (**1**–**3**) were isolated from *Swertia mileensis*. Their structures were elucidated based on extensive spectral analyses (1D and 2D NMR, MS, and IR spectroscopic means).

Keywords: secoiridoid glycoside dimers; swerilactosides A–C; *Swertia mileensis*; Gentianaceae

1. Introduction

The family Gentianaceae, annual or perennial herbs, contains about 80 genera and 700 species, of which 22 genera and 427 species are distributed in China [1]. Many species mainly belonging to the *Gentiana* and *Swertia* genus are used as traditional Chinese herbs to treat hepatitis, cholecystitis, and digestive system disease [2]. Previous investigation reveals that secoiridoid glycosides, xanthones, flavones, and triterpenoids are the main constituents of Gentianaceae plants [3]. In 1958, Fu and Sun [4] reported the isolation of three alkaloids from *Gentiana macrophylla* (namely 'Qin-Jiao' in Chinese), one of which was identified as gentianine. Afterwards, Prof. Liang *et al.* [5,6] first applied NMR and IR spectral analyses, together with chemical methods, to determine the structures of gentinidine and gentianal. Later, Govindachari *et al.* [7] proved gentianine to be an artificial product during the extraction with $NH_3{\cdot}H_2O$.

Swertia mileensis (=*Swertia leducii*), well known as 'Qing-Ye-Dan' in Chinese, belongs to the *Swertia* genus, the second largest genus next to *Gentiana* of the family Gentianaceae [8]. As a traditional Chinese medicine (TCM), it has long been used to treat viral hepatitis in the Yi and Ha-Ni nationality regions, Mile and Kaiyuan Counties, Yunnan Province. In the 1970s, a large amount of phytochemical and pharmacological investigations on *S. mileensis* was carried out, which promoted it to be documented in *Chinese Pharmacopoeia* (1977–2010 editions) as a new TCM source [9]. Presently, its significantly curative effect on acute viral hepatitis has resulted in wide clinical applications [10–13].

In order to clarify the active components [14], our previous bioassay-guided fractionation has led to the isolation of four types of novel iridoid lactones:

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swerilactones A and B (C18 skeleton) [15], swerilactones C and D (C20 skeleton) [16], swerilactones E and F (lactones with naphthyl rings), and swerilactone G (a secoiridoid aglycone dimer) [17], with anti-HBV activity *in vitro,* and subsequently, the other three unusual secoiridoid glycoside dimers (two molecules of secoiridoids connected by a molecule of the glycosyl group) were obtained from this plant. Generally, the *Swertia* genus is rich in secoiridoid glycosides; however, the secoiridoid glycoside dimers were seldom reported [3,18]. Herein, we describe the isolation and structural elucidation of swerilactosides A–C based on extensive spectroscopic analyses (Figure 1).

2. Results and discussion

Swerilactoside A (**1**) had a molecular formula of $C_{25}H_{32}O_{13}$ by positive HR-ESI-MS at *m/z* 563.1728 $[M + Na]^+$. The IR spectrum showed the absorption bands of OH (3423 cm^{-1}), C—O (1698 cm^{-1}), double bond (1620 cm^{-1}), and glycosyl group (1082, 1027, and 1005 cm^{-1}).

The ^1H and ^{13}C NMR spectra of compound **1** displayed 25 carbon signals due to 6 quaternary carbons, 11 methines, 7 methylenes, and 1 methyl group, of which two lactone carbonyl carbons, three double bonds, and one glucosyl group were revealed (Table 1).

Detailed analyses of its NMR spectra suggested a swertiamarin fragment (**1a**), which was also supported by the $^1H-^1H$ COSY, HMBC, and ROESY spectra. Compared to the known swertiamarin [19], the C-3′ in compound **1** was shifted significantly downfield from δ_C 77.7 (d) to 86.3 (d); contrarily, C-4′ was shifted slightly upfield from δ_C 71.4 (d) to 69.5 (d), which suggested that another partial structure was linked to C-3′ by the glycosidic linkage in compound **1**.

In addition to the swertiamarin fragment (**1a**), the nine residual carbons were ascribed to one lactone carbonyl carbon [δ_C 166.5 (s, C-10″)], one tetra-substituted double bond [δ_C 158.3 (s, C-5″) and 123.2 (s, C-4″)], two oxygenated methines [δ_C 95.8 (d, C-3″, dioxygenated one) and 63.4 (d, C-1″)], three methylenes [δ_C 67.4 (t, C-7″, oxygenated one), 37.3 (t, C-8″), and 29.0 (t, C-6″)], and one methyl group [δ_C 20.6 (q, C-9″)], which indicated a secoiridoid aglycone-like fragment. In the HMBC spectrum, the correlations of H-7″ with C-5″ and C-10″, H-6″ with C-4″ and C-8″, H-8″ with C-4″ and C-9″, and H-3″ with C-1″ and C-10″, together with the $^1H-^1H$ COSY correlations of H-7″/H-6″ and H-8″/H-1″/H-9″, led to the construction of the partial fragment **1b** (Figure 2).

The connection of C-3′ and C-3″ by an ether bond was determined by the HMBC correlations of H-3′ with C-3″ and H-3″

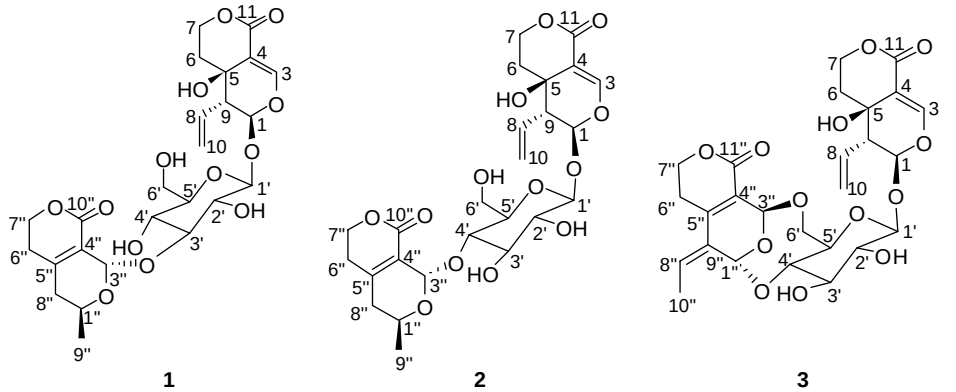

Figure 1. The structures of compounds **1**–**3**.

Table 1. ^{1}H and ^{13}C NMR spectral data of compounds **1**–**3** (in pyridine-d_5, δ in ppm, J in Hz).

	1[a]		**2**[b]		**3**[b]	
No.	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1	5.74, d, 1.2	98.7, d	5.67, d, 1.2	99.1, d	5.56, d, 1.2	99.2, d
3	7.63, s	154.4, d	7.61, s	154.8, d	7.62, s	154.6, d
4		109.2, s		108.8, s		108.9, s
5		64.3, s		64.3, s		64.3, s
6a	1.89, m	33.5, t	1.88, m	33.7, t	1.90, m	33.7, t
6b	1.74, bd, 13.4		1.72, bd, 14.0		1.74, bd, 14.1	
7a	4.73, m	65.9, t	4.72, m	66.0, t	4.74, m	65.9, t
7b	4.32, m		4.33, m		4.33, m	
8	5.42, m	133.7, d	5.39, m	133.7, d	5.42, m	133.8, d
9	2.91, dd, 9.2, 1.3	51.8, d	2.90, dd, 9.2, 1.2	51.9, d	2.90, dd, 9.5, 1.0	52.0, d
10a	5.36, dd, 17.0, 2.6	121.3, t	5.34, dd, 17.0, 2.5	121.3, t	5.37, dd, 17.0, 2.3	121.3, t
10b	5.29, dd, 9.4, 2.6		5.27, dd, 9.4, 2.5		5.28, dd, 9.6, 2.3	
11		167.9, s		168.1, s		167.9, s
1′	4.76, d, 7.9	98.7, d	4.63, d, 8.0	100.0, d	4.64, d, 8.0	100.5, d
2′	3.34, m	74.4, d	3.28, m	74.4, d	3.26, m	75.2, d
3′	3.62, t, 8.7	86.3, d	3.47, t, 9.0	76.5, d	3.44, m	75.7, d
4′	3.30, m	69.5, d	3.67, t, 9.0	78.3, d	3.77, t, 9.4	79.4, d
5′	3.41, m	78.6, d	3.37, m	77.5, d	3.40, m	72.4, d
6′a	3.90, dd, 12.0, 1.9	62.4, t	3.94, m	61.8, d	3.97, m	67.6, t
6′b	3.69, dd, 12.0, 5.4					
1″	4.34, m	63.4, d	4.41, m	63.8, d	5.78, s	95.0, d
3″	5.50, s	95.8, d	5.40, s	94.5, d	5.57, s	92.3, d
4″		123.2, s		123.2, d		119.8, s
5″		158.3, s		157.9, s		147.6, s
6″a	2.53, t, 6.3	29.0, t	2.61, m	29.4, t	2.71, m	23.3, t
6″b			2.38, m			
7″a	4.43, t, 6.4	67.4, t	4.36, m	66.9, t	4.44, m	67.0, t
7″b					4.39, m	
8″	2.28, m	37.3, t	2.27, m	37,4, t	6.53, q, 7.3	138.4, d
9″	1.26, d, 6.2	20.6, q	1.25, d, 6.2	20.6, q		130.7, s
10″		166.5, s		165.2, s	2.01, d, 7.3	14.8, q
11″						165.7, s

Notes: [a] Data measured at 400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR.
[b] Data measured at 500 MHz for ^{1}H NMR, 125 MHz for ^{13}C NMR.

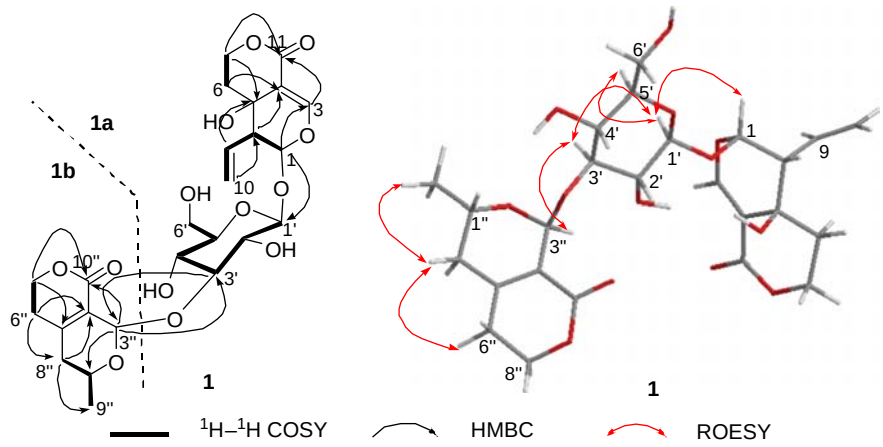

Figure 2. Selected ^{1}H–^{1}H COSY, HMBC, and ROESY correlations of compound **1**.

with C-3′. However, only a weak correlation of H-3″ with H-9″ was detected in the ROESY spectrum, which was insufficient to determine the same orientation of H-3″ and Me-9″. This problem has been encountered in our previous investigation, namely, swerilactone G possessed a similar partial structure with the fragment **1b**, and its relative configuration has been proved by X-ray single-crystal diffraction [16]. Although the Me-9 and H-3 were located at the same side, the ROESY correlation of neither H-3/H-1 nor H-3/H-9 was detected in that the connection of H—C (3)—O—C (1)—C (9) possessed the *W* conformation. In addition, the coupling constant of H-9″ ($J = 6.2$ Hz) in swerilactoside A was also identical to that of H-9 ($J = 6.2$ Hz) in swerilactone G. Thus, it was plausible to deduce that fragment **1b** possessed a similar configuration to that of **3a** in swerilactone G. Consequently, the structure of compound **1** was elucidated to be swerilactoside A, as shown in Figure 1.

Swerilactoside B (**2**) possessed the same molecular structure of $C_{25}H_{32}O_{13}$ as that of compound **1**. The UV, IR, and NMR spectra of compound **2** were very close to those of compound **1**, which suggested that they possessed a similar skeleton. The ^{1}H–^{1}H COSY and HMBC analyses suggested that compound **2** contained the same partial fragments **2a** and **2b** as those of compound **1**. The HMBC correlations of H-3″ with C-4′ and H-4′ with C-3″ and the upfield shift of C-3′ from δ_C 86.3 (d) in compound **1** to 76.5 (d) in compound **2**, as well as the downfield shift of C-4′ from δ_C 69.5 (d) in compound **1** to 78.3 (d) in compound **2**, corresponding to the variations of $\Delta\delta_{H\text{-}3'}$ (−0.15 ppm) and $\Delta\delta_{H\text{-}4'}$ (+0.37 ppm), proposed that fragment **2b** was linked to **2a** by C (4′)—O—C (3″). Similarly, the correlation of neither H-3″/H-1″ nor H-3″/H-9″ was detected in the ROESY spectrum (Figure 3), together with the completely consistent coupling constant of H-9″ ($J = 6.2$ Hz) with that in swerilactoside B and swerilactone G [17], which indicated that fragment **2b** adopted the same relative configuration as that of **1b**. Thus, the structure of compound **2** was elucidated to be swerilactoside B, as shown in Figure 1.

Swerilactoside C (**3**) had a molecular formula of $C_{26}H_{30}O_{13}$ by a quasi-molecular ion peak at *m/z* 585.1367 $[M + Cl]^-$ in the negative HR-ESI-MS. The IR spectrum suggested the presence of OH (3436 cm^{-1}), C=O (1703 cm^{-1}), double bond (1620 cm^{-1}), and glycosyl group (1084, 1057, and 1032 cm^{-1}).

The ^{1}H and ^{13}C NMR (DEPT) spectra exhibited 26 carbon resonances due to 7

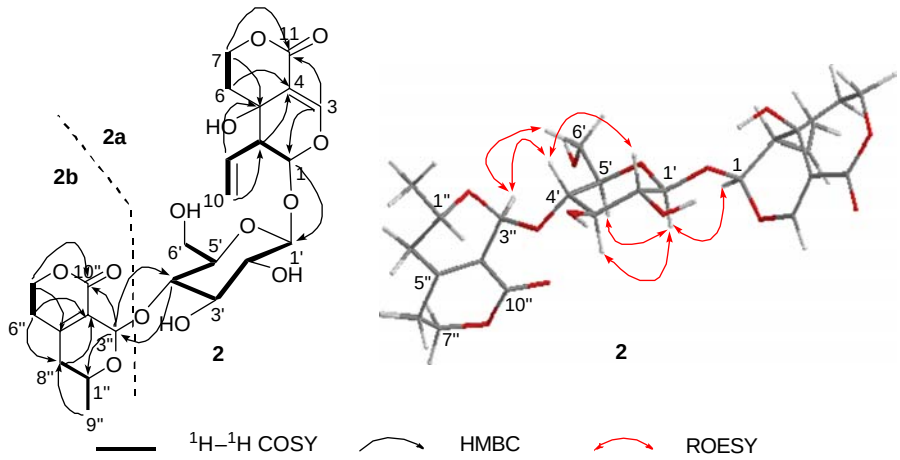

Figure 3. Selected $^{1}H-^{1}H$ COSY, HMBC, and ROESY correlations of compound **2**.

quaternary carbons, 12 methines, 6 methylenes, and 1 methyl group. The NMR spectral data of compound **3** were similar to those of compound **2**, except for the presence of additional tri-substituted double bond [δ_C 138.4 (d, C-8″) and 130.7 (s, C-9″)] and the absence of one methylene [δ_C 37.4 (t, C-8″)] observed in compound **3**, together with the obvious downfield shift of C-1″ [from δ_C 63.8 (d) in compound **2** to δ_C 95.0 (d) in compound **3**]. In addition, the chemical shift variation of C-2′ ($\Delta\delta = +0.8$ ppm), C-3′ ($\Delta\delta = -0.8$ ppm), C-5′ ($\Delta\delta = -5.1$ ppm), C-6′ ($\Delta\delta = +5.8$ ppm), and C-10″ [$\Delta\delta = -5.8$ ppm (corresponding to C-9″ in compound **2**)] was observed in Table 1. In addition to the swertiamarin fragment (**3a**), the other partial structure **3b** was constructed based on the $^{1}H-^{1}H$ COSY correlations of H-6″ with H-7″, and H-8″ with H-10″, and the HMBC correlations of H-7″ with C-5″ and C-11″, H-6″ with C-4″ and C-9″, H-8″ with C-5″ and C-1″, and H-3″ with C-1″, C-5″ and C-11″ (Figure 4). The glycosidic linkage between C-1″ and C-4′ was deduced by HMBC correlations of H-1″/C-4′ and H-4′/C-1″. Similarly, the connection of C-3″ and C-6′ by a glycosidic bond was detected by the HMBC correlations of H-3″ with C-6′ and H-6′ with C-3″.

The correlations of H-1″/H-4′ and H-3″/H-6′ in the ROESY spectrum suggested the β-orientation of H-1″ and the α-orientation of H-3″. The *Z*-configuration of the double bond between C-8″ and C-9″ was deducted based on the ROESY correlations of H-8″ with H-6″ and H-10″ with H-1″. Thus, the structure of compound **3** was deduced to be swerilactoside C, as shown in Figure 1.

Swerilactosides A–C were three unusual secoiridoid glycoside dimers obtained from the traditional Chinese herb *S. mileensis*, which further enriched the skeleton type of secoiridoid glycosides.

3. Experimental

3.1 General experimental procedures

Optical rotations were determined on a JASCO model 1020 polarimeter (Horiba, Tokyo, Japan). UV spectra were measured on a Shimadzu UV-2401A spectrophotometer (Shimadzu, Kyoto, Japan). IR (KBr) spectra were recorded on a Bio-Rad FTS-135 spectrometer (Bio-Rad, Hercules, CA, USA). 1D and 2D NMR spectra were recorded on Bruker AM-400 NMR or DRX-500 spectrometers (Bruker, Bremerhaven, Germany) with TMS as an internal standard. MS spectra were run on a VG Auto Spec-3000 spectrometer (VG, Manchester,

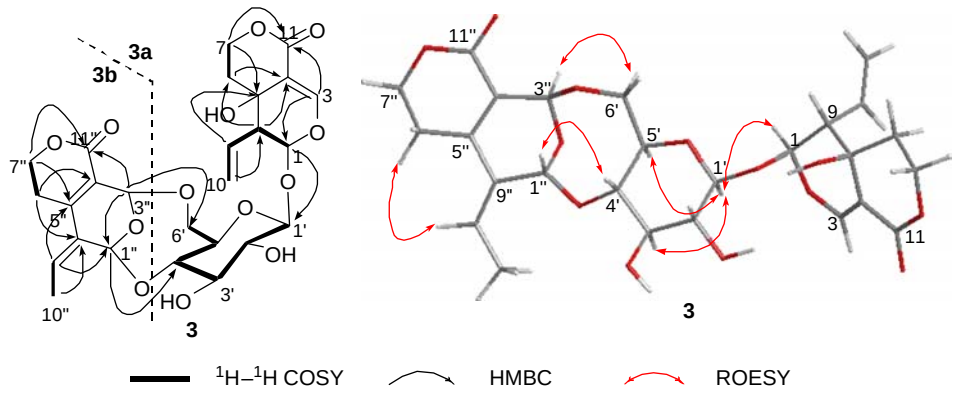

Figure 4. Selected ^{1}H–^{1}H COSY, HMBC, and ROESY correlations of compound **3**.

England). Silica gel (200–300 mesh) for column chromatography was obtained from Qingdao Makall Chemical Company, Qingdao, China. HPLC (Waters Alliance 2695), equipped with a photodiode array detector (Waters 2996) and a Waters 600 pump, was purchased from Waters Co. Ltd, Milford, MA, USA. Sephadex LH-20 (20–150 μm) was purchased from Pharmacia Fine Chemical Co. Ltd, Uppsala, Sweden.

3.2 Plant material

The whole plant of *S. mileensis* was collected in Mile County, Yunnan Province, China, on 6 November 2008, and was identified as *S. mileensis* T. N. Ho et W. L. Shi by Prof. Dr. Li-Gong Lei, Kunming Institute of Botany, Chinese Academy of Sciences. A voucher specimen (No. 2008-11-01) has been deposited in the Laboratory of Antivirus and Natural Medicinal Chemistry, Kunming Institute of Botany.

3.3 Extraction and isolation

The air-dried whole plant (5.0 kg) of *S. mileensis* was powdered and extracted with 90% and 50% EtOH under reflux successively (each time 2 h, 15.0 liters × 2 times). The combined extracts were concentrated under reduced pressure to give a residue (1.3 kg). The residue was suspended in water and extracted with petroleum ether (1.0 liters × 2), ethyl acetate (1.0 liters × 3), and *n*-butanol (1.0 liters × 3) successively. The ethyl acetate part (170.5 g) was chromatographed on a silica gel column (2.0 kg, 11.0 × 50.0 cm) eluted with $CHCl_3$–MeOH (from 100:0 to 0:100, v/v) to furnish 10 fractions A–J. Fraction B (8.5 g) was chromatographed on a silica gel column (100.0 g, 3.0 × 30.0 cm) with a gradient elution of $CHCl_3$–Me_2O (90:1 → 50:50) to supply four fractions B1–B4. Fraction B4 (3.0 g) was performed on a silica gel column (30.0 g, 1.7 × 25.0 cm) eluted with $CHCl_3$–MeOH (90:1 → 80:20) to obtain three subfractions B4-1 to B4-3. Subfraction B4-1 (100.0 mg) was dissolved in MeOH and purified with a semi-preparative HPLC apparatus, using a Waters XTerra Prep RP-18 column (7.8 × 300 mm, 10 μm), eluted with MeOH–H_2O (35:65, flow rate = 4.5 ml/min), detected at 254 nm, to obtain compound **1** (80.0 mg, Rt = 18.0 min). Subfraction B4-2 (500.0 mg) was subjected to a silica gel column (30.0 g, 1.7 × 25.0 cm) eluted with $CHCl_3$–Me_2CO (80:20), and then further purified with HPLC (the conditions were similar to compound **1**) to supply compound **2** (30.0 mg, Rt = 13.0 min). Subfraction B4-3 (300.0 mg) was first loaded on a silica gel column (30.0 g, 1.7 × 25.0 cm) and eluted with $CHCl_3$–Me_2O (80:20), and then purified

with a Sephadex LH-20 column (50.0 g, 1.4 × 145.0 cm, MeOH) to give compound **3** (100.0 mg).

3.3.1 Swerilactoside A (*1*)

A white powder; $[\alpha]_D^{19.8}$ − 94.04 (c = 0.68, MeOH); UV (MeOH) λ_{max} (nm) (log ε): 231 (4.16); IR (KBr) ν_{max} (cm^{-1}): 3423, 1698, 1620, 1473, 1419, 1280, 1269, 1082, 1027, 1005, 787; ^1H and ^{13}C NMR spectral data see Table 1; ESI-MS (+) *m/z*: 563 $[M + Na]^+$; HR-ESI-MS (+) *m/z*: 563.1728 $[M + Na]^+$ (calcd for $C_{25}H_{32}O_{13}Na$, 563.1740).

3.3.2 Swerilactoside B (*2*)

A white powder; $[\alpha]_D^{19.8}$ − 127.69 (c = 0.20, MeOH); UV (MeOH) λ_{max} (nm) (log ε): 231 (4.12); IR (KBr) ν_{max} (cm^{-1}): 3429, 1705, 1620, 1472, 1416, 1326, 1280, 1207, 1154, 1079, 1028, 948, 929, 758; ^1H and ^{13}C NMR spectral data see Table 1; ESI-MS (−) *m/z*: 575 $[M + Cl]^-$; HR-ESI-MS (−) *m/z*: 575.1517 $[M + Cl]^-$ (calcd for $C_{25}H_{32}O_{13}Cl$, 575.1531).

3.3.3 Swerilactoside C (*3*)

A white powder; $[\alpha]_D^{20.0}$ − 67.11 (c = 0.14, MeOH); UV (MeOH) λ_{max} (nm) (log ε): 269 (4.14), 240 (4.14); IR (KBr) ν_{max} (cm^{-1}): 3436, 1703, 1620, 1472, 1434, 1408, 1273, 1246, 1208, 1159, 1126, 1084, 1057, 1032, 1013, 961, 930, 903, 846, 760; ^1H and ^{13}C NMR spectral data see Table 1; ESI-MS (−) *m/z*: 585 $[M + Cl]^-$; HR-ESI-MS (−) *m/z*: 585.1367 $[M + Cl]^-$ (calcd for $C_{26}H_{30}O_{13}Cl$, 585.1374).

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