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NOTE

Rigenolides D–H, norsecoiridoid and secoiridoids from *Gentiana rigescens* Franch

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Abstract
Five new compounds, rigenolides D–H (**1**–**5**), were isolated from the aerial parts of *Gentiana rigescens* Franch. Their structures were assigned by detailed spectroscopic analyses and chemical conversions. Rigenolides D (**1**) and E (**2**) were elucidated to be a secoiridoid and a norsecoiridoid, respectively, possessing a dienone moiety in common. Rigenolides F–H (**3**–**5**) were assigned as acylated secoiridoid glucosides.

Keywords Norsecoiridoid · Secoiridoid · Secoiridoid glucoside · *Gentiana rigescens* · Rigenolides D–H

Introduction

The plants belonging to the genus *Gentiana* (Gentianaceae) contain various iridoids, secoiridoids, and their glycosides, and have been used as herbal remedies worldwide [1]. The root of *Gentiana rigescens* Franch is one of the varieties of Gentianae Radix (Long-Dan) in the Chinese Pharmacopeia, and also has been used for the treatment of hepatitis and cholecystis by the Yi ethnic minority group living in Yunnan province. In the course of our study for traditional herbal medicines used by ethnic minority groups in Yunnan province [2–5], we have reported the isolation of several secoiridoid glucosides from the aerial parts of *G. rigescens* [6, 7]. Further investigation of the aerial parts of *G. rigescens* afforded one new secoiridoid, rigenolide D (**1**), one new norsecoiridoid, rigenolide E (**2**), and three new acylated secoiridoid glucosides, rigenolides F–H (**3**–**5**). Herein, we describe the isolation and structure elucidation of **1**–**5**.

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Results and discussion

The MeOH extract obtained from the dried aerial parts of *G. rigescens* was partitioned between EtOAc and H_2O. The EtOAc-soluble materials were partitioned with *n*-hexane and 90% MeOH aq., and the 90% MeOH aq.-soluble materials were subsequently partitioned with $CHCl_3$ and 50% MeOH aq. The 50% MeOH aq.-soluble materials were separated by chromatographies repeatedly to give rigenolides D (**1**, 2 mg), E (**2**, 1 mg), F (**3**, 5 mg), G (**4**, 2 mg), and H (**5**, 1 mg), together with eight known compounds, swermacrolactone C [8], gentiolactone [9], swerilactone B [10], 2′-*O*-acetylswertiamarin [11], 2′-*O*-(2,3-dyhydroxybenzoyl)-4′-*O*-acetyl-6′-*O*-(2-hydroxy-3-*O*-β-D-glucopyranosylbenzoyl)-sweroside [12], *iso*-orientin [13]. 1-*O*-(2-Hydroxy-3-methoxybenzoyl)-β-D-glucose [14], and 3-hydroxy-1-(4-hydroxy-3-methoxyphenyl)-propan-1-one [15]. The structures of known compounds were identified by comparison of their spectroscopic data with the literature data.

Rigenolide D (**1**) was isolated as a colorless amorphous solid. The HRESIMS revealed the molecular formula of **1** to be $C_{10}H_{14}O_4$ (*m/z* 221.0793 $[M+Na]^+$, Δ + 0.3 mmu). The ^1H NMR spectrum showed the resonances due to one olefinic proton, four sp^3 methylenes, three of which were

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oxygenated, and one secondary methyl (Table 1). The ^{13}C NMR spectrum indicated the existence of ten carbons including one α,β-unsaturated carboxy group and two olefinic carbons. The gross structure of rigenolide D (**1**) was assigned by 2D NMR analysis. A ^{1}H-^{1}H COSY cross-peak of H_2-6 to H_2-7 and HMBC correlations for H_2-3 with C-4, C-5, and C-11, and for H_2-7 to C-5 and C-11 revealed the presence of an α-hydroxymethyl-α,β-unsaturated δ-lactone moiety (C-3–C-7 and C-11) (Fig. 1). The presence of a tri-substituted olefin moiety (C-1 and C-8–C-10) connected to the β-position (C-5) of the unsaturated δ-lactone was assigned by a ^{1}H-^{1}H COSY cross-peak of H-8 to H_3-10 and HMBC correlations for H_2-1 with C-5, C-8, and C-9. The existence of hydroxy groups at C-1 and C-3 was confirmed by an observation of the deuterium-induced differential isotope shifts [16] for C-1 and C-3 ($\Delta\delta_C$ each +0.11 ppm). The geometry of the double bond at C-8 was assigned as *E* by NOESY correlations for H_2-6 with H_3-10 and for H_2-1 with H-8 (Fig. 1). Therefore, the structure of rigenolide D (**1**) was elucidated as shown in Chart 1.

The HRESIMS analysis of rigenolide E (**2**) revealed the molecular formula of **2** to be $C_9H_{12}O_3$ (*m/z* 191.0688 $[M+Na]^+$, Δ +0.4 mmu). Though the ^{1}H NMR spectrum of **2** was similar to that of **1**, the resonance of an sp^2 methine in **2** was discerned in place of the signal of the hydroxymethyl group at C-4 in **1** (Table 1). This proton (H-4) showed HMBC correlations with C-11, C-5, and C-6, suggesting the lack of the hydroxymethyl group (C-3) in **2** (Fig. 1). In addition, a difference of the chemical shifts for C-1 and C-8 between **2** and **1** implied the *Z* geometry for the double bond at C-8, which was confirmed by NOESY correlations for H-8 with H_2-6 and for H_2-1 with H_3-10. Thus, the structure of rigenolide E (**2**) was assigned as shown in Chart 1.

Table 1 ^{1}H and ^{13}C NMR data for rigenolides D (**1**) and E (**2**) in CD_3OD

Position	**1**		**2**	
	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	δ_C
1	4.12 (2H, brs)	65.7	4.38 (2H, s)	56.6
3	4.19 (2H, s)	57.9		
4	–	129.2	6.09 (1H, br s)	114.1
5	–	155.8	–	158.1
6	2.56 (2H, t, 6.0)	29.9	2.65 (2H, td, 6.3, 0.9)	25.9
7	4.41 (2H, t, 6.0)	67.1	4.40 (2H, t, 6.3)	67.6
8	5.73 (1H, qt, 7.0, 1.0)	125.1	6.34 (1H, q, 7.2)	135.4
9	–	139.8	–	138.4
10	1.59 (3H, dt, 7.0, 1.0)	14.7	1.94 (3H, d, 7.2)	14.5
11	–	167.1	–	168.6

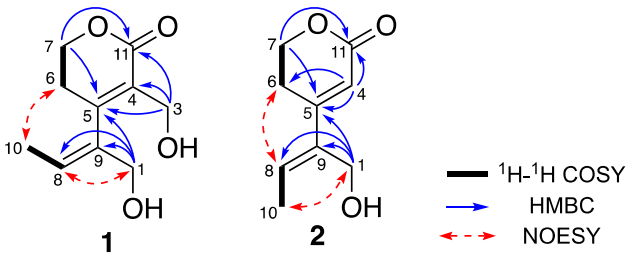

Fig. 1 Selected 2D NMR correlations for rigenolides D (**1**) and E (**2**)

Rigenolides F (**3**) and G (**4**) were isolated individually as optically active colorless amorphous solids {$[\alpha]_D$ –178.0 (*c* 0.44, MeOH) for **3**; $[\alpha]_D$ –162.3 (*c* 0.18, MeOH) for **4**}. The HRESIMS of **3** and **4** revealed their molecular formulae to be $C_{18}H_{24}O_{10}$ and $C_{20}H_{26}O_{11}$, respectively (*m/z* 423.1261 $[M+Na]^+$, Δ –0.6 mmu for **3**; *m/z* 465.1387 $[M+Na]^+$, Δ +1.4 mmu for **4**). In addition to the ^{1}H NMR signals similar to sweroside [17, 18], a representative secoiridoid glucoside of the *Gentiana* plants, **3** and **4** showed one and two acetyl signals, respectively (Table 2). These findings suggested that **3** and **4** were mono- and diacetyl derivatives of sweroside, respectively. The down-field shifted chemical shifts for H-2′ (δ_H 4.68) in **3** and for H-2′ (δ_H 4.68) and H_2-6′ (δ_H 4.42 and 4.22) in **4** compared with those for sweroside indicated the presence of the acetyl groups at C-2′ position in **3** and at C-2′ and C-6′ positions in **4**. Rigenolides F (**3**) and G (**4**) were individually treated with acetic anhydride in pyridine to give acetylated derivatives (**3a** and **4a**). The ^{1}H NMR data and specific rotation values for **3a** and **4a**

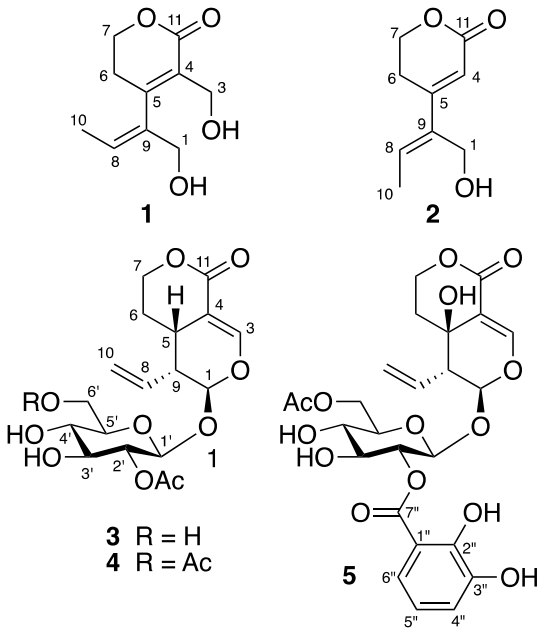

Chart 1 The structures of rigenolides D–H (**1**–**5**)

Table 2 ^{1}H and ^{13}C NMR data for rigenolides F–H (**3**–**5**) in CD_3OD

Position	**3**		**4**		**5**	
	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	δ_C	δ_H (*J* in Hz)	δ_C
1	5.46 (d, 2.0)	98.3	5.33 (d, 1.8)	98.5	5.51 (d, 1.5)	100.0
3	7.57 (d, 2.5)	153.6	7.56 (d, 2.5)	153.5	7.09 (s)	153.4
4	–	106.5	–	106.6	–	109.4
5	2.88 (ddt, 13.0, 5.7, 2.5)	28.7	2.89 (ddt, 13.0, 5.6, 2.2)	28.7	–	64.3
6	1.77 (dq, 13.0, 2.5)	25.8	1.77 (dq, 13.0, 2.2)	25.8	1.77 (td, 12.0, 4.9)	33.5
	1.67 (qd, 13.0, 4.5)		1.67 (tdd, 13.0, 13.0, 4.3)		1.69 (m)	
7	4.45 (ddd, 11.0, 4.5, 2.5)	70.0	4.46 (ddd, 11.3, 4.3, 2.2)	70.0	4.67 (ddd, 12.0, 11.0, 2.6)	65.7
	4.33 (ddd, 13.0, 11.0, 2.5)		4.33 (ddd, 13.0, 11.3, 2.2)		4.23 (ddd, 11.0, 4.9, 1.6)	
8	5.51 (dt, 17.0, 10.0)	132.9	5.51 (dt, 17.1, 10.0)	132.9	5.31 (m)	133.2
9	2.68 (ddd, 10.0, 5.7, 2.0)	43.4	2.69 (ddd, 10.0, 5.6, 1.8)	43.5	2.90 (dd, 8.6, 1.5)	51.9
10	5.31 (dd, 17.0, 2.0)	121.1	5.32 (dd, 17.1, 1.7)	121.2	5.37 (dd, 16.5, 2.8)	121.5
	5.27 (dd, 10.0, 2.0)		5.27 (dd, 10.0, 1.7)		5.26 (dd, 9.5, 2.8)	
11	–	168.1	–	168.1	–	166.8
1′	4.85 (d, 8.0)	97.7	4.88 (d, 8.1)	97.8	5.01 (d, 8.1)	99.0
2′	4.68 (dd, 9.0, 8.0)	74.9	4.68 (dd, 9.4, 8.1)	74.7	4.98 (dd, 9.0, 8.1)	75.6
3′	3.56 (t, 9.0)	75.5	3.56 (t, 9.4)	75.3	3.80 (t, 9.0)	75.0
4′	3.35 (m)	71.5	3.39 (t, 9.4)	71.3	3.50 (dd, 9.8, 9.0)	71.3
5′	3.37 (ddd, 9.0, 6.0, 2.0)	78.5	3.57 (m)	75.7	3.67 (ddd, 9.8, 5.3, 2.1)	75.9
6′	3.90 (dd, 12.0, 2.0)	62.6	4.42 (dd, 12.0, 2.1)	64.4	4.46 (dd, 12.0, 2.1)	64.2
	3.67 (dd, 12.0, 6.0)		4.22 (dd, 12.0, 5.4)		4.28 (dd, 12.0, 5.3)	
1″					–	113.3
2″					–	151.7
3″					–	147.4
4″					7.02 (dd, 8.0, 1.5)	122.4
5″					6.76 (t, 8.0)	120.2
6″					7.38 (dd, 8.0, 1.5)	121.1
7″						171.8
2′-OAc	1.98 (3H, s)	171.8	1.99 (3H, s)	171.8		
		21.0		21.0		
6′-OAc			2.07 (3H, s)	172.7	2.09 (3H, s)	172.7
				20.7		20.7

were identical to those for tetraacetylsweroside [19] in each case. Accordingly, the structures of rigenolides F (**3**) and G (**4**) were elucidated to be 2′-*O*-acetylsweroside and 2′,6′-di-*O*-acetylsweroside, respectively.

Rigenolide H (**5**) was obtained as an optically active colorless amorphous solid {$[\alpha]_D$ −76.1 (*c* 0.12, MeOH)}, and its molecular formula $C_{25}H_{28}O_{14}$ was estimated by the HRESIMS (*m/z* 575.1357 $[M+Na]^+$, Δ −2.0 mmu). The 1D NMR spectra of **5** displayed the signals corresponding to swertiamarin [20, 21] along with the resonances due to one acetyl group and one 2,3-dihydroxybenzoyl group (Table 2). The presence of the acetyl group at C-6′ position and the 2,3-dihydroxybenzoyl group at C-2′ position was revealed by HMBC analysis and down-field shifted chemical shifts for H-2′ (δ_H 4.98) and H_2-6′ (δ_H 4.46 and 4.28). Acetylation of **5** furnished a pentaacetyl derivative (**5a**), whose ^{1}H NMR spectrum and specific rotation value were identical to those of peracetyl derivative prepared from 2′-(2,3-dihydroxybenzoyl)-swertiamarin [6]. Therefore, the structure of rigenolide H (**5**) was assigned as 6′-*O*-acetyl-2′-*O*-(2,3-dihydroxybenzoyl)-swertiamarin.

The aerial parts of *G. rigescens* were investigated to give one new secoiridoid, rigenolide D (**1**), one new norsecoiridoid, rigenolide E (**2**), and three new secoiridoid glucosides, rigenolides F–H (**3**–**5**). Among others, rigenolide E (**2**) had a unique norsecoiridoid structure, whereas a regioisomer **2** has been reported as a metabolite derived from gentiopicroside by a microbial biotransformation using the endophytic fungus [22].

Experimental

General

Optical rotations were measured by a JASCO P-2200 digital polarimeter. MS were obtained on a Waters LCT PREMIER 2695. NMR spectra were measured by a Bruker AVANCE-500 instrument using tetramethylsilane as an internal standard. Column chromatography was performed with silica gel 60 N (63–210 μm, Kanto Kagaku, Japan), Diaion HP-20 (Mitsubishi Chemical, Japan), MCI gel CHP 20P (75–150 μm, Mitsubishi Chemical), Sephadex LH-20 (25–100 μm, GE Health Care, UK), YMC-pack ODS-A (S-50 μm, YMC Co., Ltd., Japan). HPLC was carried out with Mightysil RP-18GP (250 × 20 mm, 5 μm, Kanto Kagaku), Mightysil RP-18GPII (250 × 20 mm, 5 μm), COSMOSIL Cholester (250 × 20 mm, 5 μm, Nacalai Tesque, Inc. Japan), and COSMOSIL πNAP (250 × 20 mm, 5 μm, Nacalai Tesque, Inc.).

Plant material

Gentiana rigescens Franch. ex Hemsl. was purchased in August, 2008, in Yunnan Province, China, and identified by Professor Li-Shan Xie of the Kunming Institute of Botany, Chinese Academy of Sciences, China. Voucher specimens (08JY0007) were deposited in the herbarium of Tokushima University.

Extraction and isolation

The aerial parts of *G. rigescens* (1.9 kg, dry) were crushed and extracted with MeOH at room temperature for 3 days to give the extract (354 g), which was partitioned between EtOAc and H_2O. The EtOAc-soluble materials were further partitioned with *n*-hexane and 90% MeOH aq., and the 90% MeOH aq.-soluble materials were subsequently partitioned with $CHCl_3$ and 50% MeOH aq. The 50% MeOH aq.-soluble materials were subjected to chromatography over an MCI gel CHP20P column [MeOH/H_2O (0:1 to 1:0)] to give 14 fractions (frs.1–14). Fr. 5 was fractioned by SiO_2 column chromatography {$CHCl_3$/MeOH (30:1 to 0:1)} to yield ten fractions (frs. 5.1–10). Fr. 5.3 was purified by reversed-phase HPLC {COSMOSIL Cholester, MeOH/H_2O (15:85)} to give swermacrolactone C (3 mg). Rigenolide D (**1**, 2 mg) was isolated from fr. 5.4 using ODS HPLC {Mightysil PR-18GP, MeOH/H_2O (15:85)}. Repeated column chromatographies of fr. 6 on a silica gel {$CHCl_3$/MeOH (30:1 to 0:1)}, an ODS {MeOH/H_2O (3:7 to 1:0)}, followed by a silica gel {$CHCl_3$/EtOAc (10:1 to 0:1)} gave frs. 6.1–6.5. Purification of fr. 6.3 by ODS HPLC {Mightysil RP-18GPII, MeOH/H_2O (17:83)} furnished rigenolide E (**2**, 1 mg). Crystallization of fr. 7 with $CHCl_3$ gave *iso*-orientin (15 mg), and the mother liquor was separated by silica gel column chromatography {$CHCl_3$/MeOH (1:1 to 0:1)} to yield 12 fractions (frs. 7.1–12). Fr. 7.2 was separated by ODS column chromatography {MeOH/H_2O (4:6 to 1:0)} to afford four fractions (frs. 7.2.1–7.2.4). Purification of fr. 7.2.1 by reversed-phase HPLC {COSMOSIL Cholester, MeOH/H_2O (20:80)} gave gentiolactone (4 mg). 3-Hydroxy-1-(4-hydroxy-3-methoxyphenyl)–propan-1-one (5 mg) was isolated from fr. 7.2.2 by reversed-phase HPLC {COSMOSIL πNAP, MeOH/H_2O (35:65)}. Fr. 7.8 was chromatographed over a silica gel column {$CHCl_3$/acetone (10:1 to 0:1)} to afford eight fractions (frs. 7.8.1–8). Fr. 7.8.5 was purified by reversed-phase HPLC {COSMOSIL πNAP, MeOH/H_2O (50:50)} to yield rigenolide F (**3**, 5 mg) and 2′-*O*-acetylswertiamarin (9 mg), while purification of fr. 7.8.6 by the same condition gave 1-*O*-(2-hydroxy-3-methoxybenzoyl)-β-D-glucose (7 mg). Fr. 9 was chromatographed over a silica gel column {EtOAc/MeOH (1:0 to 0:1)} and an ODS column {MeOH/H_2O (0:1 to 1:0)}, and purified by reversed-phase HPLC {COSMOSIL Cholester, MeOH/H_2O (20:80)} to afford swerilactone B (4 mg). Fr. 10 was separated by an ODS column {MeOH/H_2O (4:6 to 1:0)} to give 17 fractions (frs. 10.1–17). Fr. 10.9 was fractionated by silica gel column chromatography {$CHCl_3$/MeOH (30:1 to 0:1)}, and purified by reversed-phase HPLC {COSMOSIL Cholester, MeOH/H_2O (40:60)} to furnish rigenolide H (**5**, 1 mg). Rigenolide G (**4**, 2 mg) was isolated from fr. 10.10 by ODS HPLC {Mightysil RP-18GP, MeOH/H_2O (45:55)}. Fr. 10.13 was repeatedly chromatographed over a Sephadex LH-20 column [MeOH/H_2O (1:0 to 0:1)] and a silica gel column [$CHCl_3$/MeOH (30:1 to 0:1)], and purified by reversed-phase HPLC on COSMOSIL Cholester [MeOH/H_2O (52:48)] to give 2′-*O*-(2,3-dyhydroxybenzoyl)-4′-*O*-acetyl-6′-*O*-(2-hydroxy-3-*O*-β-D-glucopyranosylbenzoyl)-sweroside (11 mg).

Rigenolide D (1)

White amorphous solid; HRESIMS *m/z* 221.0793 $[M+Na]^+$ (calcd for $C_{10}H_{14}O_4Na$, 221.0790); UV (MeOH) λ_{max} 216 (ε 3800) nm; IR (KBr) υ_{max} 3385, 2921, and 1701 cm^{-1}; ^1H and ^{13}C NMR (CD_3OD) (Table 1).

Rigenolide E (2)

White amorphous solid; HRESIMS *m/z* 191.0688 $[M+Na]^+$ (calcd for $C_9H_{12}O_3Na$, 191.0684); UV (MeOH) λ_{max} 266 (ε 9800) nm; IR (KBr) υ_{max} 3383, 2928, and 1712 cm^{-1}; ^1H and ^{13}C NMR (CD_3OD) (Table 1).

Rigenolide F (3)

White amorphous solid; $[\alpha]_D^{17}$ −178.0 (*c* 0.44, MeOH); HRESIMS *m/z* 423.1261 $[M+Na]^+$ (calcd for $C_{18}H_{24}O_{10}Na$, 423.1267); UV (MeOH) λ_{max} 243 (ε 8100) nm; IR (KBr) υ_{max} 3398, 2924, 1740, and 1691 cm^{-1}; ^1H and ^{13}C NMR (CD_3OD) (Table 2).

Rigenolide G (4)

White amorphous solid; $[\alpha]_D^{25}$ −162.3 (*c* 0.18, MeOH); HRESIMS *m/z* 465.1387 $[M+Na]^+$ (calcd for $C_{20}H_{26}O_{11}Na$, 465.1373); UV (MeOH) λ_{max} 242 (ε 8500) nm; IR (KBr) υ_{max} 3376, 2925, 1740, and 1705 cm^{-1}; ^1H and ^{13}C NMR (CD_3OD) (Table 2).

Rigenolide H (5)

White amorphous solid; $[\alpha]_D^{18}$ −76.1 (*c* 0.12, MeOH); HRESIMS *m/z* 575.1357 $[M+Na]^+$ (calcd for $C_{25}H_{28}O_{14}Na$, 575.1377); ^1H and ^{13}C NMR (CD_3OD) (Table 2).

Acetylation of rigenolides F–H (3–5) and 2′-*O*-(2,3-dihydroxybenzoyl)-swertiamarin (6)

Rigenolides F and G (**3** and **4**, each 1.0 mg) were treated with acetic anhydride (500 μL) and dry pyridine (500 μL) at room temperature for 6 h. The reaction mixtures were evaporated to afford peracetyl derivatives (**3a**, 1.3 mg; **4a**, 1.1 mg). Peracetyl derivatives (**5a**, 1.0 mg; **6a**, 0.8 mg) of rigenolide H (**5**) and 2′-*O*-(2,3-dihydroxybenzoyl)-swertiamarin (**6**), which was previously isolated from the same origin by our group [6], were prepared in the same manner. The ^1H NMR data and specific rotation values for **3a** and **4a** were consistent with the literature data for tetraacetylsweroside [18], while those for **5a** were coincident with **6a**.

Peracetyl rigenolide F (3a) {= peracetyl rigenolide G (4a)}

Pale yellow amorphous solid; $[\alpha]_D^{28}$ −170.9 (*c* 0.14, $CHCl_3$); HRESIMS *m/z* 549.1592 $[M + Na]^+$ (calcd for $C_{24}H_{30}O_{13}Na$, 549.1584); ^1H NMR ($CDCl_3$) δ_H 7.56 (1H, d, *J* = 1.6 Hz, H-3), 5.47 (1H, dd, *J* = 17.0, 9.8 Hz, H-8), 5.32 (1H, d, *J* = 1.6 Hz, H-1), 5.30 (1H, dd, *J* = 17.0, 1.4 Hz, H-10a), 5.28 (1H, dd, *J* = 9.8, 1.4 Hz, H-10b), 5.24 (1H, t, *J* = 9.6 Hz, H-3′), 5.09 (1H, t, *J* = 9.6 Hz, H-4′), 5.00 (1H, dd, *J* = 9.6, 8.1 Hz, H-2′), 4.91 (1H, d, *J* = 8.1 Hz, H-1′), 4.45 (1H, dt, *J* = 10.8, 3.0 Hz, H-7a), 4.32 (1H, m, H-7b), 4.30 (1H, dd, *J* = 12.6, 4.5 Hz, H-6′a), 4.15 (1H, dd, *J* = 12.6, 2.0 Hz, H-6′b), 3.75 (1H, ddd, *J* = 9.6, 4.5, 2.0 Hz, H-5′), 2.87 (1H, m, H-5), 2.69 (1H, dd, *J* = 9.8, 1.4 Hz, H-9), 2.09, 2.03, 2.00, 1.97 (each 3H, s, OAc), and 1.71 (2H, m, H-6).

Peracetyl rigenolide H (5a) {= 2′-*O*-(2,3-dihydroxybenzoyl)-swertiamarin pentaacetate (6a)}

Pale yellow amorphous solid; $[\alpha]_D^{20}$ − 51.0 (*c* 0.10, MeOH); HRESIMS *m/z* 743.1767 $[M + Na]^+$ (calcd for $C_{33}H_{36}O_{18}Na$, 743.1799); ^1H NMR (CD_3OD) δ_H 7.80 (1H, dd, *J* = 8.0, 1.4 Hz, H-6″), 7.50 (1H, dd, *J* = 8.0, 1.4 Hz, H-4″), 7.36 (1H, t, *J* = 8.0 Hz, H-5″), 7.27 (1H, s, H-3), 5.55 (1H, d, *J* = 1.5 Hz, H-1), 5.50 (1H, t, *J* = 9.0 Hz, H-3′), 5.38 (1H, dd, *J* = 15.7, 2.7 Hz, H-10a), 5.34 (1H, m, H-8), 5.27 (1H, dd, *J* = 9.4, 2.7 Hz, H-10b), 5.18 (1H, d, *J* = 9.0 Hz, H-1′), 5.15 (1H, t, *J* = 9.0 Hz, H-4′), 5.12 (1H, t, *J* = 9.0 Hz, H-2′), 4.69 (1H, td, *J* = 11.8, 2.8 Hz, H-7a), 4.34 (1H, dd, *J* = 12.5, 4.5 Hz, H-6′a), 4.27 (1H, ddd, *J* = 11.8, 4.9, 1.6 Hz, H-7b), 4.20 (1H, dd, *J* = 12.5, 4.5 Hz, H-6′b), 4.04 (1H, ddd, *J* = 9.0, 4.5, 2.1 Hz, H-5′), 2.92 (1H, dd, *J* = 9.6, 1.5 Hz, H-9), 2.31, 2.28, 2.07, 2.02, 1.94 (each 3H, s, OAc), 1.80 (1H, ddd, 13.5, 11.8, 4.9 Hz, H-6a), and 1.71 (1H, m, H-6b).

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