Sesquiterpenes and Dimers Thereof from *Chloranthus fortunei*

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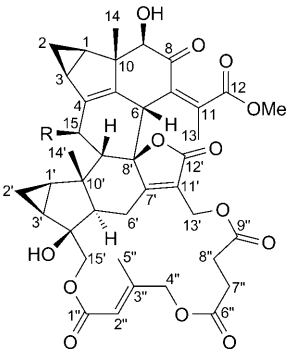
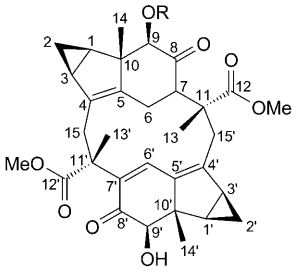
Four new compounds, including one new sesquiterpene dimer, *i.e.*, shizukaol P (**1**), one new dimeric sesquiterpene glycoside, *i.e.*, 9-*O*-*β*-glucopyranosylcycloshizukaol A (**2**), and two new sesquiterpenes, *i.e.*, shizukanolides G and H (**3** and **4**, resp.), together with eight known compounds, were isolated from the aerial part of *Chloranthus fortunei*. The structures and relative configurations were elucidated on the basis of spectroscopic data and by comparison with those of the related compounds reported in the literature.

Introduction. – *Chloranthus*, a genus of the Chloranthaceae family, is mainly distributed in the east of Asia [1]. Previous work on this genus indicated that sesquiterpenes [2–14] and sesquiterpene oligomers [14–24] are their major secondary metabolites. Recently, diterpenoids have also been reported from this genus [11]. The sesquiterpene dimers were reported to exhibit antifungal activity [21], anti-tumor activity [11], potent and selective inhibition on the delayed rectifier (I_K) K^+ current [21][23], and inhibition on the expression of cell adhesion molecules [25]. *Chloranthus fortunei* (A. Gray) SOLMS-LAUB has been used in Chinese folk medicine for the treatment of bone fractures [26]. During our ongoing search for biologically active substances from this plant, 13 compounds have been isolated from the aerial part of it. Four of them were new compounds, including one new sesquiterpene dimer, *i.e.*, shizukaol P (**1**), one new dimeric sesquiterpene glycoside, *i.e.*, 9-*O*-*β*-glucopyranosylcycloshizukaol A (**2**), and two new sesquiterpenes, *i.e.*, shizukanolides G and H (**3** and **4**, resp.). The other eight known compounds were identified as shizukaol F (**5**) [18], yinxiancaol (**6**) [14], chloramultilide B (**7**) [22], cycloshizukaol A (**8**) [17], chloranthalactone C (**9**) [4][9], shizukanolide C (**10**) [4], shizukanolide F (**11**) [7], and chloranoside A (**12**) [10]. Their structures and relative configurations were elucidated on the basis of their spectroscopic data and by comparing with the related compounds reported in the literature.

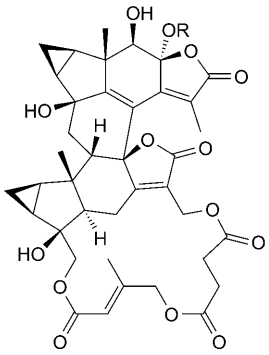
Results and Discussion. – Compound **1** was obtained as a white powder. The ESI-MS spectrum showed the *pseudo*-molecular ion at *m*/*z* 771.3 ($[M+Na]^+$), and the molecular formula was determined as $C_{40}H_{44}O_{14}$ from the HR-ESI-MS (*m*/*z* 771.2632 $[M+Na]^+$; calc. 771.2629), indicating 19 degrees of unsaturation. IR Absorptions



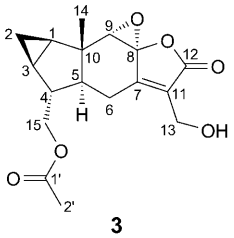
1 R = OH
5 R = H



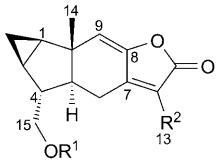
2 R = glucosyl
8 R = H



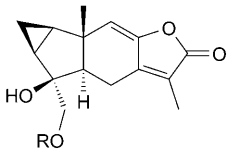
6 R = Me
7 R = H



3



4 R^1 = Ac, R^2 = CH_2OH
9 R^1 = Ac, R^2 = Me
10 R^1 = H, R^2 = Me
11 R^1 = H, R^2 = CH_2OH



12 R = glucosyl

revealed the presence of OH (3438.5 cm^{-1}) and C=O (1739.5 cm^{-1}) functionalities. The ^{13}C-NMR and DEPT spectroscopy revealed 40 C-atom signals, which were ascribed to six C=O groups, eight olefinic C-atoms, one MeO, four Me, eight CH_2, and nine CH groups, and four quaternary C-atoms (including two oxygenated quaternary C-atoms) (*Table 1*). The ^{1}H,^{1}H-COSY spectrum of **1** showed two units with each for H-atoms with a coupling pattern corresponding to a 1,2-disubstituted cyclopropane ring (δ(H) 0.46–0.54 (*m*), 1.08–1.15 (*m*), 1.92–1.96 (*m*), and 2.06–2.12 (*m*); 0.67–0.77 (*m*), 1.22–1.26 (*m*), 1.30–1.40 (*m*), and 1.46–1.58 (*m*)). The characteristic high-field CH_2 signals of **1** at δ(H) 0.46–0.54 (*m*, H_β–C(2)) were diagnostic for the cyclopropane ring of a lindenane sesquiterpene [3–6]. Therefore, **1** appeared to be a lindenane dimer from the genus *Chloranthus*. The NMR data (*Table 1*) of **1** were quite similar to those of shizukaol F (**5**) [18], a significant difference was that **1** had a OH substituent at C(15) (δ(C) 65.2), which could be confirmed by the HMBC correlations observed between H–C(3), H–C(4), H–C(5), H–C(15), and H–C(9′) (*Fig.*). Thus, the structure of **1** was established as 15-hydroxyshizukaol F. The relative configuration of **1** was elucidated from ROESY correlations, including H–C(1)/H–C(3), H–C(1)/H_α–C(2), H–C(1′)/H–C(3′), H–C(1′)/H_α–C(2′), H_α–C(2′)/H–C(3′), H–C(1)/H–C(9), H–C(9)/H–C(5′), which were α-oriented, so the 9-OH was β-oriented. The other ROESY correlations of H–C(6)/Me(13), H–C(6)/Me(14), H_β–C(6′)/Me(14′),

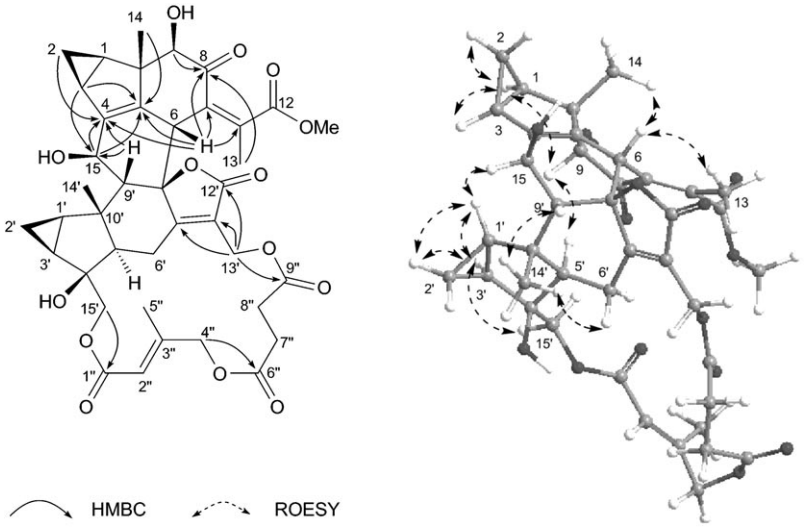


Figure. *Key correlations in the HMBC and ROESY spectra of shizukaol P* (**1**)

H–C(9′)/Me(14′) were also observed. The ROESY interactions of H–C(15)/H_α–C(1′) and H_α–C(3′)/CH_2(15′) suggested that HO–C(15) and HO–C(4′) were both β-oriented. Hence, the structure of **1** was determined to be as shown and named shizukaol P.

Compound **2** was obtained as a yellowish powder, its HR-ESI-MS (positive-ion mode) exhibited a *pseudo*-molecular ion peak at *m/z* 733.2833 ($[M+Na]^+$; calc. 733.2836), ascribable to a molecular formula $C_{38}H_{46}O_{13}$. The IR spectrum showed absorption bands at $\tilde{\nu}_{max}$ 3426.9 and 1724.1 cm^{-1}, indicating the presence of OH and C=O groups. A typical signal was observed in the ^{1}H-NMR spectrum (*Table 1*) of **2** at δ(H) 4.58 (*d*, $J = 8.4$), attributed to the anomeric H-atom of a sugar unit with β-linkage. The corresponding anomeric C-atom signal appeared at δ(C) 100.7 in the HMQC spectrum. A β-glucosyl moiety was established by ^{1}H,^{1}H-COSY, HMQC, and HMBC spectra, and further confirmed by the acidic hydrolysis of **2** in 10% aq. HCl/dioxane solution at 80° for 4 h, which resulted in a release of glucose, identified by TLC comparison of the hydrolysate with the authentic sugar sample. The remaining 32 C-atom signals of **2** (*Table 1*) were very similar to those of cycloshizukaol A (**8**), which was also isolated from *C. japonicus* [17]. The difference was that cycloshizukaol A has a symmetric structure, whereas compound **2** had two sets of similar signals. The aglycone of **2** was determined to be cycloshizukaol A by a comprehensive analysis of the 1D- and 2D-NMR spectra. The β-glucosyl moiety was linked unambiguously with C(9), based on the HMBC correlations of H–C(1″)/C(9) and H–C(9)/C(1″). Hence, the structure of **2** was determined as a new dimeric sesquiterpene glycoside, 9-*O*-β-glucopyranosylcycloshizukaol A. This is the first time that a dimeric sesquiterpene glycoside was reported. The relative configuration of **2** was also elucidated by the ROESY experiment.

Compound **3** was obtained as a yellow powder with the molecular formula $C_{17}H_{20}O_6$ as deduced from the HR-ESI-MS (*m/z* 343.1156 $[M+Na]^+$; calc. 343.1158), which

Table 1. *^{1}H- and ^{13}C-NMR Data* (300 and 100 MHz, $CDCl_3$) *of Compounds* **1** *and* **2**. δ in ppm, J in Hz.

	1		**2**	
	δ(H)	δ(C)	δ(H)	δ(C)
H–C(1)	2.06–2.12 (*m*)[a])	25.9	1.92–1.98 (*m*)	24.7
H_α–C(2)	1.08–1.15 (*m*)	16.5	0.94–1.00 (*m*)	14.8
H_β–C(2)	0.46–0.54 (*m*)		0.27 (*d*, *J* = 3.6)	
H–C(3)	1.92–1.96 (*m*)	3.6	2.10–2.16 (*m*)[a])	27.2
C(4)		145.0		149.6
C(5)		137.4		136.5
H–C(6)	4.10 (*s*)	41.5	6.92 (*s*)	139.5
C(7)		130.3		138.9
C(8)		199.8		199.1
H–C(9)	3.93 (*s*)	79.5	3.94 (*s*)	80.9
C(10)		51.4		56.1
C(11)		147.9		46.9
C(12)		170.1		175.9
Me(13)	1.90 (*s*)	23.6	1.49 (*s*)	28.1
Me(14)	1.06 (*s*)	15.2	1.08 (*s*)	16.9
H_a–C(15)	4.93 (*s*)	65.2	3.25 (*d*, *J* = 13.8)	39.1
H_b–C(15)			2.16 (*d*, *J* = 13.8)	
MeO–C(12)	3.75 (*s*)	52.5	3.64 (*s*)	52.1
H–C(1′)	1.46–1.58 (*m*)	25.6	1.80–1.83 (*m*)	25.7
H_α–C(2′)	0.67–0.77 (*m*)	11.6	0.86–0.88 (*m*)	14.3
H_β–C(2′)	1.22–1.26 (*m*)		0.21 (*d*, *J* = 3.6)	
H–C(3′)	1.30–1.40 (*m*)	27.5	2.16–2.20 (*m*)[a])	27.3
C(4′)		77.3		148.5
H–C(5′) or C(5′)	1.80–1.88 (*m*)	59.1		136.9
CH_2(6′) or H–C(6′)	2.60–2.64 (*m*), 2.78–2.83 (*m*)	24.4	6.92 (*s*)[a])	139.2
C(7′)		173.1		139.1
C(8′)		92.1		198.7
H–C(9′)	2.01 (*s*)	61.8	3.57 (*s*)	81.2
C(10′)		43.8		55.7
C(11′)		123.6		46.9
C(12′)		170.9		175.9
CH_2(13′) or Me(13′)	4.91 (*d*, *J* = 12.9), 4.70 (*d*, *J* = 12.9)	55.1	1.49 (*s*)[a])	28.6
Me(14′)	0.86 (*s*)	25.9	1.05 (*s*)	16.3
H_a–C(15′)	4.80 (*d*, *J* = 12.0)	71.0	3.28 (*d*, *J* = 12.6)	39.2
H_b–C(15′)	3.47 (*d*, *J* = 12.0)		2.15[a])	
MeO–C(12′)			3.63 (*s*)	52.2
C(1″) or H–C(1″)		166.1	4.58 (*d*, *J* = 8.4)	100.7
H–C(2″)	5.96 (*s*)	112.7	2.95 (*t*, *J* = 8.4, 8.4)	72.5
C(3″) or H–C(3″)		154.1	3.53 (*t*, *J* = 9.0, 9.0)	75.5
CH_2(4″) or H–C(4″)	5.08 (*d*, *J* = 17.1), 4.35 (*d*, *J* = 17.1)	65.5	3.93[a])	67.7
Me(5″) or H–C(5″)	2.13 (*s*)	15.6	3.34 (*d*, *J* = 9.0)	76.6
C(6″) or CH_2(6″)		171.6	3.78, 3.88 (each 1 H)	60.7
H_a–C(7″)	2.98–3.00 (*m*)	29.0		
H_b–C(7″)	2.56–2.60 (*m*)			
H_a–C(8″)	2.80–2.84 (*m*)[a])	28.9		
H_b–C(8″)	2.76–2.78 (*m*)[a])			
C(9″)		171.9		

[a]) Overlapped signals.

indicated eight degrees of unsaturation. The IR spectrum revealed the presence of OH (3453.9 cm^{-1}) and C=O (1778.1, 1739.5 cm^{-1}) groups. Four H-atom signals appeared at δ(H) 0.69–0.74 (*m*), 0.78–0.84 (*m*), 1.22–1.32 (*m*), and 1.55–1.62 (*m*), which indicated the presence of a cyclopropane ring. This was evidenced by the ^{1}H,^{1}H-COSY spectrum. The ^{1}H- and ^{13}C-NMR (*Table 2*) were quite similar to those of shizukanolide D [7], which indicated that **3** was a lindenane sesquiterpene. The differences were that the Me(13) signal of shizukanolide D was absent and an O–CH_2 group appeared at δ(H) 4.16 (*dd*), along with a corresponding C-atom signal appeared at δ(C) 55.5, which indicated that C(13) could be substituted with a OH group. Thus, compound **3** was concluded to be 13-hydroxyshizukanolide D, and confirmed by ^{1}H,^{1}H-COSY and HMBC experiments. The relative configuration of **3** was determined by ROESY experiments. ROESY Correlations including H–C(1)/H–C(3), H–C(1)/ H_α–C(2), H–C(3)/ H–C(5), H–C(3)/CH_2(15), H–C(5)/CH_2(15) were observed, which were assigned to be α-oriented. The other ROESY interactions of H_β–C(2)/H–C(4) and H_β–C(6)/Me(14) revealed that they were in β-configuration. The epoxide ring was established to be α-oriented by the ROESY correlation between H–C(9) and Me(14). Hence, the structure of **3** was determined, and it was named shizukanolide G.

Table 2. *^{1}H- and ^{13}C-NMR Data* (300 and 100 MHz, $CDCl_3$) *of Compounds* **3** *and* **4**. δ in ppm, *J* in Hz.

	3		**4**	
	δ(H)	δ(C)	δ(H)	δ(C)
H–C(1)	1.22–1.32 (*m*)	24.7	1.47–1.55 (*m*)	27.0
H_α–C(2)	0.69–0.74 (*m*)	16.8	0.73–0.80 (*m*)	16.7
H_β–C(2)	0.78–0.84 (*m*)		0.80–0.86 (*m*)	
H–C(3)	1.55–1.62 (*m*)	22.5	1.22–1.32 (*m*)	22.0
H–C(4)	1.51–1.55 (*m*)	42.5	1.65–1.76 (*m*)	42.5
H–C(5)	2.54–2.63 (*m*)	48.7	2.20–2.26 (*m*)	59.9
H_α–C(6)	2.70–2.74 (*m*)	22.6	2.80–2.90 (*m*)	22.6
H_β–C(6)	2.20–2.32 (*m*)		2.27–2.40 (*m*)	
C(7)		155.9		149.0
C(8)		88.2		150.6
H–C(9)	4.38 (*s*)	64.7	6.33 (*s*)	124.1
C(10)		42.6		41.6
C(11)		131.0		122.6
C(12)		169.6		170.0
CH_2(13)	4.09–4.16 (*m*)	55.5	4.39 (*s*)	54.4
Me(14)	0.74 (*s*)	16.3	0.87 (*s*)	20.7
CH_2(15)	4.14–4.18 (*m*)	66.1	4.16 (*d*, *J* = 6.0)	65.7
C(1′)		171.4		171.2
Me(2′)	2.04 (*s*)	21.1	2.05 (*s*)	20.7

Compound **4** was obtained as a white powder with the molecular formula $C_{17}H_{20}O_5$ as deduced from its HR-ESI-MS (*m*/*z* 327.1212 ($[M+Na]^+$; calc. 327.1208)). Compound **4** was also recognized as a lindenane sesquiterpene from its ^{1}H- and ^{13}C-NMR data (*Table 2*), which were quite similar with those of **3**, except that the epoxide ring was replaced by a C=C bond assigned to be C(8) = C(9) in **4**; a corresponding olefinic H-atom appeared at δ(H) 6.33 (*s*, H–C(9)) instead of the O–CH at δ(H) 4.38 (*s*) in **3**.

Comparing the NMR data of **4** with those of chloranthalactone C (**9**) [9], compound **4** was determined as 13-hydroxychloranthalactone C and confirmed by the key HMBC correlations of H–C(9)/C(1), H–C(9)/C(7), H–C(9)/C(14), H–C(6)/C(8), CH_2(13)/C(8), H–C(1)/C(9), H–C(5)/C(9), Me(14)/C(9). The relative configuration of **4** was also determined by ROESY experiment. The structure of **4** was accordingly established, and it was named shizukanolide H.

Comparison of the NMR and MS data with literature values showed that the known compounds were shizukaol F (**5**) [18], yinxiancaol (**6**) [14], chloramultilide B (**7**) [22], cycloshizukaol A (**8**) [17], chloranthalactone C (**9**) [4][9], shizukanolide C (**10**) [4], shizukanolide F (**11**) [7], and chloranoside A (**12**) [10].

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Experimental Part

General. All solvents used were of anal. grade (*Shanghai Chemical Plant*, Shanghai, P. R. China). HPLC: *Waters 2695* Separation Module, equipped with a *Waters 2996* photodiode array detector and a *Kromacil C18* column (4.6 × 150 mm, 0.5 μm). Column chromatography (CC): SiO_2 *H* (200–300 mesh; *Qingdao Marine Chemical Ltd.*, Qingdao, P. R. China); *MCI* gel *CHP 20P* (75–150 μm; *Mitsubishi Chemical Ind.*, Tokyo, Japan); *Sephadex LH-20* (25–100 μm; *Pharmacia*); *RP-18* (20–45 μm; *Fuji Silysia Chemical Ltd.*). TLC: SiO_2 GF_{254} (*Yantai Huiyou Inc.*, Yantai, P. R. China). Optical rotations: *Perkin-Elmer 341* polarimeter. UV Spectra: *Shimadzu UV-2450* UV-VIS spectrophotometer; λ_{max} (log ε) in nm. IR Spectra: *Nicolet FT-IR 750* spectrophotometer; in cm^{-1}. ^{1}H- (300 MHz) and ^{13}C-NMR (100 MHz) Spectra: *Bruker AMX-300/400* spectrometer; δ in ppm, J in Hz, with Me_4Si as internal standard. ESI-MS: *Bruker Esquire 3000 plus* spectrometer. HR-ESI-MS: *Micromass Q-Tof Global* mass spectrometer.

Plant Material. The aerial part of *C. fortunei* was collected from Zhangzhu Town, Yixing City, Jiangsu Province, China, in May 2007 and identified by Prof. *Gui-Xin Chou* (Shanghai R&D Center for Standardization of Chinese Medicines). A voucher sample (20070531) was deposited with the Shanghai Research Center for Modernization of Traditional Chinese Medicine, Shanghai Institute of Materia Medica, Shanghai, China.

Extraction and Isolation. The aerial part of *C. fortunei* (2 kg) was extracted with 95% EtOH at r.t. The extract was concentrated under reduced pressure to obtain a crude extract (138 g), which was suspended in H_2O, then partitioned with AcOEt to isolate the AcOEt soluble compounds (72 g). These were then subjected to a column of *MCI* gel eluted with 30, 85, and 100% aq. MeOH, and 33 g of the 85% aq. MeOH fraction were chromatographed over a SiO_2 column (petroleum ether (PE)/acetone, 10:1 to 1:5), *Sephadex LH-20* ($CHCl_3$/MeOH, 1: 1), and a series of *RP-18* columns (50–70% aq. MeOH) to yield shizukaol P (**1**, 18 mg), 9-*O*-*β*-glucopyranosylcycloshizukaol A (**2**, 15 mg), shizukanolide G (**3**, 42 mg), shizukanolide H (**4**, 80 mg), shizukaol F (**5**, 87 mg), yinxiancaol (**6**, 12 mg), chloramultilide B (**7**, 32 mg), cycloshizukaol A (**8**, 64 mg), chloranthalactone C (**9**, 190 mg), shizukanolide C (**10**, 105 mg), shizukanolide F (**11**, 15 mg), and chloranoside A (**12**, 22 mg).

Shizukaol P (= *Methyl (2Z)-2-[(1a*R,*1b*S,*2*R,*4a*R,*4b*R,*8a*R,*9*S,*9a*S,*10a*R,*10b*S,*10c*R,*11*R,*11b*S,*15*E*)-1a,1b,2,3,4a,6,8,8a,9,9a,10,10a,10b,10c,11,11b-Hexadecahydro-2,9,11-trihydroxy-1b,10b,16-trimethyl-3,6,14,19,22-pentaoxo-9,7-(methanooxybut[2]enooxybutanooxymethano)cyclopropa[4,5]cyclopropa[4′,5′]cyclopenta[1′,2′:7,8]acephenanthryleno[10a,10-*b*]furan-4(1*H*)-ylidene]propanoate*; **1**). White powder. $[\alpha]_D^{20} = -71.0$ ($c = 0.2$, MeOH). UV (MeOH): 220 (4.28). IR (KBr): 3438.5, 2927.5, 1739.5, 1664.3, 1436.7, 1375.0, 1272.8, 1222.7, 1159.0, 1085.7. ^{1}H- and ^{13}C-NMR: *Table 1*. ESI-MS: 771.3 ($[M + Na]^+$), 747.6 ($[M - H]^-$). HR-ESI-MS: 771.2632 ($[M + Na]^+$, $C_{40}H_{44}NaO_{14}^+$; calc. 771.2629).

9-O-β-Glucopyranosylcycloshizukaol A (= *Dimethyl (1aS,3R,6S,6aR,7aS,9R,12S,12aR,13R,15S)-1,1a,2,3,4,5,6,6a,7,7a,8,9,12,12a-Tetradecahydro-13-hydroxy-15-(glucopyranosyloxy)-3,6,9,12-tetramethyl-14,16-dioxo-4,6:10,12-diethanobiscyclopropa[3,4]cyclopenta[1,2-a:1′,2′-g]cyclododecene-3,9-dicarboxylate*; **2**). Yellowish powder. $[\alpha]_D^{20} = +172.7$ ($c = 0.3$, MeOH). UV (MeOH): 222 (4.10), 341 (3.77). IR (KBr): 3426.9, 2935.2, 1724.1, 1670.1, 1623.8, 1457.9, 1375.0, 1286.3, 1238.1, 1141.7, 1076.1, 1039.5. ^{1}H- and ^{13}C-NMR: *Table 1*. ESI-MS: 733.4 ($[M+Na]^+$). HR-ESI-MS: 733.2833 ($[M+Na]^+$, $C_{38}H_{46}NaO_{13}^+$; calc. 733.2836).

Shizukanolide G (= *[(1aS,5aS,6R,6aS,7aR,7bS,7cS)-5,5a,6,6a,7,7a,7b,7c-Octahydro-4-(hydroxymethyl)-7b-methyl-3-oxo-3H-cyclopropa[2,3]oxireno[4,5]indeno[5,6-b]furan-6-yl]methyl Acetate*; **3**). Yellow powder. $[\alpha]_D^{20} = -144$ ($c = 0.2$, MeOH). UV (MeOH): 226 (4.02). IR (KBr): 3453.9, 3008.5, 2941.0, 1778.1, 1739.5, 1440.6, 1382.7, 1367.3, 1249.7, 1008.6, 943.0, 756.0. ^{1}H- and ^{13}C-NMR: *Table 2*. ESI-MS: 343.2 ($[M+Na]^+$). HR-ESI-MS: 343.1156 ($[M+Na]^+$, $C_{17}H_{20}NaO_6^+$; calc. 343.1158).

Shizukanolide H (= *[(4aS,5R,5aS,6aR,6bS)-2,4,4a,5,5a,6,6a,6b-Octahydro-3-(hydroxymethyl)-6b-methyl-2-oxocyclopropa[2,3]indeno[5,6-b]furan-5-yl]methyl Acetate*; **4**). White powder. $[\alpha]_D^{20} = -127.3$ ($c = 0.3$, MeOH). UV (MeOH): 283 (4.47). IR (KBr): 3459.7, 2996.9, 2902.4, 1751.1, 1731.8, 1635.4, 1367.3, 1242.0, 1027.9, 838.9. ^{1}H- and ^{13}C-NMR: *Table 2*. ESI-MS: 327.1 ($[M+Na]^+$). HR-ESI-MS: 327.1212 ($[M+Na]^+$, $C_{17}H_{20}NaO_5^+$; calc. 327.1208).

Acid Hydrolysis of Compound **2** [27]. Compound **2** (2 mg) was dissolved in 10% aq. HCl/dioxane (1:1), and then heated at 80° for 4 h in a H_2O bath. After cooling, the reaction mixtures were neutralized with Ag_2CO_3, filtered, extracted with $CHCl_3$ (3×1 ml), and then concentrated. The H_2O layer (monosaccharide portion) was examined by TLC, and compared with an authentic glucose sample ($CHCl_3$/MeOH/H_2O, 5:4:1).

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