Two New Diterpenoid Glucosides from *Clerodendrathus spicatus*

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Two new diterpenoid glucosides, clerodendranthusides B and C (**1** and **2**, resp.), together with 16 known compounds, comprising four lignans, five miscellaneous phenylpropanoids, two flavonoids, one sesquiterpenoid glycoside, two triterpenoid glycosides, one megastigmane, as well as one anthraquinone, were isolated from the 50% EtOH extract of the whole plants of *Clerodendrathus spicatus*. Their structures were elucidated by chemical and spectroscopic methods.

Introduction. – *Clerodendrathus spicatus* (THUNB.) C. Y. WU ex H. W. LI (Lamiaceae), also called renal tea, is a traditional medicinal plant growing in Southeast Asia [1], which has been widely used in treating chronic nephritis, hepatitis, jaundice, urinary lithiasis, and biliary lithiasis [2]. Previous studies on this plant disclosed the presence of flavonoids, polyphenolic acids, and diterpenes [1–6]. Our phytochemical investigation on the 50% EtOH extract of the title plant led to the isolation of 18 compounds, comprising clerodendranthuside B (**1**), a new 8β-hydroxyisopimarene-type diterpenoid glucoside, and clerodendranthuside C (**2**), a new rearranged abietanoid-type diterpenoid glucoside, along with sixteen known compounds including four lignans, *i.e.*, syringaresinol [7], syringaresinol 4′-*O*-β-glucopyranoside [8], 1-hydroxysyringaresinol [9], and 8-hydroxypinoresinol [10], five miscellaneous phenylpropanoids, *i.e.*, 2,6,2′,6′-tetramethoxy-4,4′-bis(2,3-epoxy-1-hydroxypropyl)biphenyl [11], albibrissinoside B [12], glypentoside C [13], ethyl caffeate [14], and (2*S*,*E*)-*N*-[2-hydroxy-2-(4-hydroxyphenyl)ethyl]ferulamide [15], two flavonoids, *i.e.*, prunin [16] and (2*S*)-naringenin [17], one sesquiterpenoid glycoside, amarantholidol A glycoside [18], two triterpenoid glycosides, *i.e.*, arjunglucoside I [19] and arjungenin-23,28-bis-*O*-glucopyranoside [20], one megastigmane, *i.e.*, vomifoliol [21], and one anthraquinone, *i.e.*, emodin [22]. Except for prunin, (2*S*)-naringenin, and vomifoliol, the above other compounds were reported from this genus for the first time. In this article, we report the isolation and structural elucidation of compounds **1** and **2** (*Fig. 1*).

Results and Discussion. – Clerodendranthuside B (**1**) had the molecular formula $C_{26}H_{42}O_{11}$ as deduced from the HR-ESI-MS (found: $[M+Na]^+$ at m/z 553.2646). A *doublet* signal at δ(H) 4.20 ($J = 7.0$ Hz) (*Table*) combined with the acid hydrolysis experiment, disclosed a β-glucopyranosyl group. The structure of **1** was established to

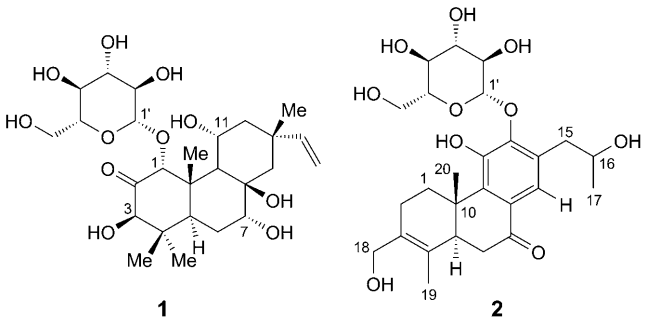

Fig. 1. *The structures of compounds* **1** *and* **2**

Table. *^{1}H- and ^{13}C-NMR Data of* **1** *and* **2** (in CD_3OD)

	δ(H) of **1**	δ(H) of **2**	δ(C) of **1**	δ(C) of **2**
H–C(1) or CH_2(1)	4.47 (*s*)	1.58 (*td*, *J* = 12.3, 6.8, H_α), 3.50 (br. *d*, *J* = 12.0, H_β)	92.3 (*d*)	32.9 (*t*)
C(2) or CH_2(2)	–	2.34 (br. *t*, *J* = 13.0), 2.27 (br. *d*, *J* = 13.4)	214.5 (*s*)	27.0 (*t*)
H–C(3) or C(3)	4.70 (*s*)	–	80.8 (*d*)	132.5 (*s*)
C(4)	–	–	46.5 (*s*)	130.3 (*s*)
H–C(5)	2.42 (br. *d*, *J* = 11.7)	2.80 (br. *d*, *J* = 13.2)	41.7 (*d*)	47.1 (*d*)
CH_2(6)	1.58 (*dt*, *J* = 13.6, 1.8, H_α), 2.13 (*td*, *J* = 13.6, 1.8, H_β)	2.84 (*dd*, *J* = 15.0, 3.2), 2.50 (*dd*, *J* = 15.0, 12.8)	26.3 (*t*)	38.2 (*t*)
H–C(7) or C(7)	3.41 (br. *s*)	–	75.7 (*d*)	201.0 (*s*)
C(8)	–	–	78.2 (*s*)	130.6 (*s*)
H–C(9) or C(9)	2.15 (*d*, *J* = 10.6)	–	48.0 (*d*)	140.0 (*s*)
C(10)	–	–	47.9 (*s*)	39.4 (*s*)
H–C(11) or C(11)	4.26 (*td*, *J* = 10.8, 3.7)	–	68.2 (*d*)	150.0 (*s*)
CH_2(12) or C(12)	1.45 (*t*, *J* = 11.8, H_α), 1.70 (*dt*, *J* = 12.3, 2.6, H_β)	–	49.0 (*t*)	150.9 (*s*)
C(13)	–	–	38.3 (*s*)	133.1 (*s*)
CH_2(14) or H–C(14)	1.96 (*d*, *J* = 14.3, H_α), 1.13 (*dd*, *J* = 14.3, 2.0, H_β)	7.46 (*s*)	47.3 (*t*)	122.4 (*d*)
H–C(15) or CH_2(15)	5.76 (*dd*, *J* = 17.5, 10.7)	1.97 (*dd*, *J* = 13.2, 6.6), 1.65 (*dd*, *J* = 13.2, 6.6)	152.6 (*d*)	41.2 (*t*)
CH_2(16) or H–C(16)	4.82 (br. *d*, *J* = 10.7), 4.90 (br. *d*, *J* = 17.5)	4.10 (*sext*, *J* = 6.4)	109.4 (*t*)	68.7 (*d*)
Me(17)	1.26 (*s*)	1.12 (*d*, *J* = 6.2)	25.9 (*q*)	23.2 (*q*)
Me(18) or CH_2(18)	0.69 (*s*)	4.01 (*d*, *J* = 12.0), 4.18 (*d*, *J* = 12.0)	16.7 (*q*)	63.3 (*t*)
Me(19)	1.13 (*s*)	1.75 (*s*)	29.7 (*q*)	15.8 (*q*)
Me(20)	1.08 (*s*)	1.28 (*s*)	15.5 (*q*)	16.2 (*q*)
H–C(1′)	4.20 (*d*, *J* = 7.0)	4.60 (*d*, *J* = 7.8)	105.5 (*d*)	107.9 (*d*)
H–C(2′)	3.28–3.38 (*m*)	3.28 (*t*, *J* = 8.0)	78.6 (*d*)	78.9 (*d*)
H–C(3′)	3.25–3.30 (*m*)	3.45 (*t*, *J* = 8.5)	71.7 (*d*)	71.2 (*d*)
H–C(4′)	3.10–3.14 (*m*)	3.43 (*t*, *J* = 8.3)	78.3 (*d*)	78.3 (*d*)
H–C(5′)	3.28–3.33 (*m*)	3.52 (br. *t*, *J* = 8.5)	75.4 (*d*)	75.7 (*d*)
CH_2(6′)	3.77 (*dd*, *J* = 12.1, 2.2), 3.60 (*dd*, *J* = 12.1, 5.4)	3.83 (*dd*, *J* = 12.0, 2.3), 3.75 (*dd*, *J* = 12.0, 4.7)	62.9 (*t*)	62.5 (*t*)

be (1α,3β,7α,11α,13α)-3,7,8,11-tetrahydroxy-2-oxopimar-15-en-1-yl β-D-glucopyranoside by means of NMR analysis.

The ^{1}H-NMR spectrum of **1** displayed four Me *singlet*s (δ(H) 0.69, 1.08, 1.13, and 1.26), a vinyl *ABX* (5.76 (*dd*, J = 17.5, 10.7), 4.90 (br. *d*, J = 17.5), and 4.82 (br. *d*, J = 10.7)), and signals of four O-bearing CH groups (4.70 (*s*), 4.47 (*s*), 4.26 (*td*, J = 10.8, 3.7), and 3.41 (br. *s*)). The ^{13}C-NMR and DEPT spectra (*Table*) of **1** showed one glucopyranosyl moiety and the aglycone with 20 C-signals: four Me, three CH_2, six sp^3 CH groups, four sp^3 quaternary C-atoms, one CO group (δ(C) = 214.5) and one C=C bond (δ(C) 109.4 and 152.6). The above evidences suggested an 8β-hydroxyisopimarene-type diterpenoid glucoside [23].

The combined analysis of the HMQC and HMBC spectra of **1** (*Fig. 2*) determined the positions of the CO group and of the four O-bearing CH groups as C(2), C(1), C(3), C(7), and C(11), resp. The presence of HO–CH(11) rather than HO–CH(12) was also corroborated by the CH ^{1}H signal which showed as *triplet* of *doublet*s (J = 10.8, 3.7 Hz) and NOE cross-peaks of Me(20)/H–C(11) (*Fig. 3*). Furthermore, the shift of the signal for C(1) at δ(C) 92.3 and HMBC cross-peaks of H–C(1′)/C(1) indicated the glucopyranosyl group to be attached on C(1). The signal of H–C(7) observed as a broad *singlet* disclosed that it was in equatorial (β) orientation in the chair-form ring *B* (*Fig. 3*). In the NOESY experiments (*Fig. 3*), axial Me(20) showed significant NOE correlations with H–C(1), H–C(11), and Me(19), suggesting that both H–C(1) and H–C(11) were in β-configuration. H–C(3) was elucidated to be α-oriented on the basis of NOE cross-peaks of H–C(3)/H–C(5), and H–C(3)/Me(18).

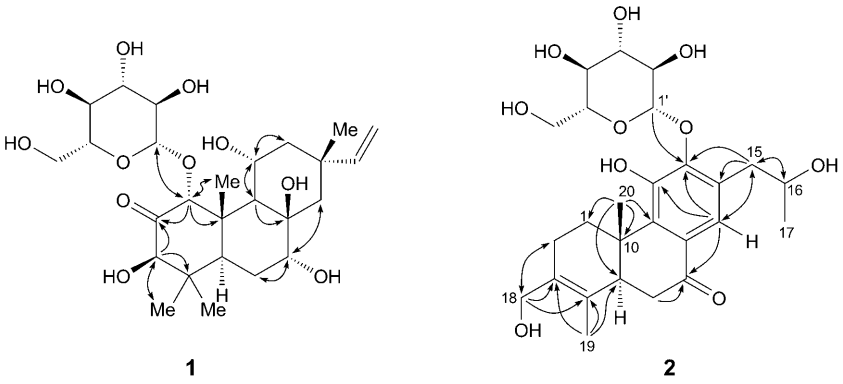

Fig. 2. *The key HMBCs* (H → C) *of* **1** *and* **2**

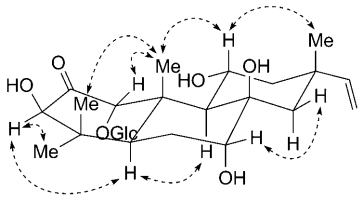

Fig. 3. *The significant NOESY correlations of* **1**

Clerodendranthuside C (**2**) was obtained as a colourless amorphous powder. The HR-ESI-MS spectrum showed a *quasi*-molecular ion peak $[M+Na]^+$ at *m/z* 531.2189, according to the molecular formula $C_{26}H_{36}O_{10}$. The acid hydrolysis experiment gave glucose as the sugar moiety. The detailed NMR studies (*Table*) allowed us to elucidate the structure of **2** to be 12-[(*β*-glucopyranosyl)oxy]-11,16,18-trihydroxy-17(15 → 16)-18(4 → 3)-*abeo*-abieta-3,8,11,13-tetraen-7-one.

The ^{1}H- and ^{13}C-NMR spectra of **2** displayed signals of a *β*-glucopyranosyl moiety (δ(H) 4.60 (*d*, *J* = 7.8); δ(C) 107.9, 78.9, 78.3, 75.7, 71.2, and 62.5) and 20 C-atom signals for the aglycone unit. The latter was resolved into one aromatic ring (δ(H) = 7.46, *s*; δ(C) 150.9, 150.0, 140.0, 133.1, 130.6, and 122.4), one C=C bond (δ(C) 132.5 and 130.3, each *s*), one ketone (δ(C) 201.0, *s*), two tertiary Me groups (δ(H) 1.28 and 1.75), one HO−CH_2 group (δ(H) 4.18 and 4.01, each *d*, *J* = 12.0; δ(C) 63.3, *t*), a 2-hydroxyprop-1-yl group (δ(H) 1.97 (*dd*, *J* = 13.2, 6.6, 1 H), 1.65 (*dd*, *J* = 13.2, 6.6, 1 H), 4.10 (*sext*, *J* = 6.4, 1 H), and 1.12 (*d*, *J* = 6.2, 3 H)), as well as three CH_2 groups and one CH group, as well as one sp^3 quaternary C-atom, suggesting an abieta-8,11,13-triene diterpenoid glucoside [24].

Based on the diterpenoid skeleton, the HMQC and HMBC spectra of **2** (*Fig. 2*) constructed the structure of **2**. In which, the ketone was positioned as C(7), a phenolic OH group, the glucosyloxy, and the 2-hydroxypropyl groups were located on C(11), C(12), and C(13) of the aromatic ring, respectively. Two Me groups were placed on C(10) and C(4), the latter and the HO−CH_2 group were linked with the isolated C=C bond. Consequently, a rearranged abietanoid-type diterpenoid glucoside was defined. The NOESY correlations of Me−C(10)/H_β−C(6), H−C(5)/H_α−C(1) confirmed the configuration of **2** as shown in *Fig. 1*.

Experimental Part

General. Column chromatography (CC): silica gel (SiO_2; 200–300 mesh; *Qingdao Haiyang, Co.*, P. R. China), *D1400* macroporous resin (*Yangzhou Pharmaceutical Factory*, P. R. China), *Sephadex LH-20* (*Pharmacia Biotech AB*, Uppsala, Sweden), *MCI gel CHP-20P* (*Mitsubishi Chemical Industries Co., Ltd.*, Japan), and *ODS-A gel* (*Greenberbs Science & Technology Development Co., Ltd.*, Beijing, P. R. China). TLC: silica gel *HSGF$_{254}$* (*Yantai Jiangyou Guijiao Kaifa Co.*, P. R. China). HPLC Analyses: *Waters* HPLC system, *Waters-51-HPLC* pump, *PL-ELS 1000* detector (*Polymer Laboratories*, UK), column: *Prevail Carbohydrate ES 5 μ*, i.d. 4.6 × 250 mm. Optical rotation: *Perkin-Elmer 341* polarimeter. UV Spectra: *Shimadzu UV-2550* spectrophotometer. IR Spectra: *Nicolet-Magna-750-FTIR* spectrometer; KBr pellets; in cm^{-1}. NMR Spectra: *Bruker AV-400* instrument at 400 (^{1}H) and 100 MHz (^{13}C); in CD_3OD or (D_6)DMSO soln.s; *δ* in ppm rel. to Me_4Si; *J* in Hz. ESI-MS and HR-ESI-MS: *Bruker Esquire 3000plus* and a *Finnigan LC QDECA* mass spectrometers, resp.; in *m/z* (rel. int.).

Plant Material. The fresh whole plant of *Clerodendrathus spicatus* (Lamiaceae) was collected in the south of Yunnan Province, P. R. China, in October 2006. The plant was identified by Dr. *Ji Huang* of Shanghai Institute of Materia Medica. A voucher specimen (No. 06-10-05) was deposited with the Herbarium of Shanghai Institute of Materia Medica.

Extraction and Isolation. The dry whole herbs of *C. spicatus* (5 kg) were extracted with 20 l 50% EtOH 3 d at r.t. 3 ×. The concentrated extract was subjected to CC (*D1400* macroporous resin, ∅ 10 × 65 cm; H_2O, then 10, 30, 50 % (*v*/*v*) EtOH). The 30% EtOH fraction (78 g) was subjected to CC (SiO_2, 2.0 kg; $CHCl_3$/MeOH 30 : 1, 20 : 1, 15 : 1, 10 : 1, 8 : 1, 4 : 1, 1 : 1): *Frs. 1–7*. *Fr. 1* was subjected to CC (*MCI* gel *CHP-20P*; H_2O, then 20, 40, 60, 80, 100% (*v*/*v*) MeOH): *Frs. 1.1–1.6*. 2,6,2′,6′-Tetramethoxy-4,4′-bis(2,3-epoxy-1-hydroxypropyl)biphenyl (7 mg), ethyl caffeate (28 mg), and (2*S*,*E*)-*N*-[2-hydroxy-2-(4-hydroxyphenyl)ethyl]ferulamide (9 mg) were obtained from *Fr. 1.2*, *Fr. 1.3*, and *Fr. 1.5*, resp., after repeated CC

(1. *Sephadex LH-20*; H_2O; 2. *LiChrospher RP-C18*; MeOH/H_2O 0, 10, 20, 30, 40%). *Fr. 2* was subjected to CC *(MCI* gel *CHP-20P*; MeOH/H_2O 0, 20, 40, 60, 80, 100%): *Frs. 2.1–2.6*. Repeated CC (1. *Sephadex LH-20*; H_2O; 2. *LiChrospher RP-C18*; MeOH/H_2O 25%) on *Fr. 2.4* gave **1** (12 mg). *Fr. 2.5* furnished 8-hydroxypinoresinol (6 mg) and albibrissinoside B (14 mg) after repeated CC (1. *Sephadex LH-20*; H_2O; 2. *LiChrospher RP-C18*; MeOH/H_2O 5, 10, 15, 20, 25%). Vomifoliol (5 mg) was obtained from *Fr. 2.6* through repeated CC (1. *Sephadex LH-20*; H_2O; 2. *LiChrospher RP-C18*; MeOH/H_2O 35%). *Fr. 3* was subjected to CC *(MCI* gel *CHP-20P*; MeOH/H_2O 0, 20, 40, 60, 80, 100%): *Frs. 3.1–3.6*. Syringaresinol 4′-*O*-*β*-glucopyranoside (17 mg) was isolated by CC (*LiChrospher RP-C18*; MeOH/H_2O 30%) from *Fr. 3.2*. *Fr. 4* was subjected to CC *(MCI* gel *CHP-20P*; MeOH/H_2O 0, 20, 40, 60, 80, 100%): *Frs. 4.1–4.4*. Amarantholidol A glycoside (11 mg) was obtained by CC (*LiChrospher RP-C18*; MeOH/H_2O 25%) from *Fr. 4.3*. *Fr. 5* was subjected to CC *(MCI* gel *CHP-20P*; MeOH/H_2O 0, 20, 40, 60, 80, 100%): *Frs. 5.1–5.7*. *Fr. 5.2* yielded **2** (8 mg) and 1-hydroxysyringaresinol (2 mg) after repeated CC (1. *Sephadex LH-20*; H_2O; 2. *LiChrospher RP-C18*; MeOH/H_2O 0, 5, 10, 15, 20%). *Fr. 6* was subjected to CC (*MCI* gel *CHP-20P*; MeOH/H_2O 0, 20, 40, 60, 80, 100%): *Frs. 6.1–6.4*. Glypentoside C (5 mg) and prunin (8 mg) were purified from *Fr. 6.3* after CC (*LiChrospher RP-C18*; MeOH/H_2O 0, 5, 10, 15, 20%). *Fr. 7* was subjected to CC *(MCI* gel *CHP-20P*; MeOH/H_2O 0, 20, 40, 60, 80, 100%): *Frs. 7.1–7.4*. *Fr. 7.3* provided arjunglucoside I (11 mg) and arjungenin-23,28-bis-*O*-glucopyranoside (8 mg) *via* CC (*LiChrospher RP-C18*; MeOH/H_2O 0, 5, 10, 15, 20%). The 50% EtOH fraction (13 g) was subjected to CC (SiO_2, 0.5 kg; $CHCl_3$/MeOH 50:1, 30:1, 10:1, 5:1, 1:1): *Frs. A–E*. *Fr. B* was subjected to CC *(MCI* gel *CHP-20P*; MeOH/H_2O 0, 20, 40, 60, 80, 100%): *Frs. B.1–B.4*. Syringaresinol (12 mg) was purified by CC (*LiChrospher RP-C18*; MeOH/H_2O 35%) from *Fr. B.3*. *Fr. C* was subjected to CC (*MCI* gel *CHP-20P*; MeOH/H_2O 0, 20, 40, 60, 80, 100%): *Frs. C.1–C.4*. (2*S*)-Naringenin (4 mg) and emodin (18 mg) were obtained from *Fr. C.3* after CC (*LiChrospher RP-C18*; MeOH/H_2O 0, 5, 10, 15, 20%).

Clerodendranthuside B (*=(1α,3β,7α,11α,13α)-3,7,8,11-Tetrahydroxy-2-oxopimar-15-en-1-yl β*-D-*Glucopyranoside*; **1**). Colorless amorphous powder. $[\alpha]_D^{25} = -13.2$ ($c = 0.600$, MeOH). IR: 3423, 2925, 1716, 1635, 1396, 1072. ^{1}H- and ^{13}C-NMR: *Table*. ESI-MS (pos.): 553.3 ($[M+Na]^+$), 1083.4 ($[2M+Na]^+$). ESI-MS (neg.): 575.4 ($[M+HCOO]^-$), 1059.4 ($[2M-H]^-$). HR-ESI-MS: 553.2646 ($[M+Na]^+$, $C_{26}H_{42}NaO_{11}^+$; calc. 553.2625).

Clerodendranthuside C (*=12-[(β-Glucopyranosyl)oxy]-11,16,18-trihydroxy-17(15→16)-18(4→3)-*abeo-*abieta-3,8,11,13-tetraen-7-one = (4b*S*,8a*S*)-4b,5,6,8a,9,10-Hexahydro-4-hydroxy-7-(hydroxymethyl)-2-(2-hydroxypropyl)-4b,8-dimethyl-10-oxophenanthren-3-yl β*-D-*Glucopyranoside*; **2**). Colorless amorphous powder. $[\alpha]_D^{25} = -3.0$ ($c = 0.200$, MeOH). UV (MeOH): 215 (15600), 274 (6040), 324 (2020). IR: 3406, 2926, 1670, 1601, 1427, 1329, 1066. ^{1}H- and ^{13}C-NMR: *Table*. ESI-MS (pos.): 531.3 ($[M+Na]^+$), 1039.5 ($[2M+Na]^+$). ESI-MS (neg.): 507.1 ($[M-H]^-$). HR-ESI-MS: 531.2189 ($[M+Na]^+$, $C_{26}H_{36}NaO_{10}^+$; calc. 531.2206).

Acid Hydrolysis of **1** *and* **2**. Each sample (2 mg) of **1** and **2** was treated with 2N aq. HCl at 90° for 4 h. The mixture was neutralized with $NaHCO_3$, and then extracted with BuOH. The aq. soln. was analyzed by ELSD-HPLC (column: *Prevail Carbohydrate ES 5* μ, 5 μm, i.d. 4.6 × 250 mm; MeCN/H_2O 80%; flow rate 1.0 ml/min; r.t.). Glucose (standard: t_R 17.5 min; **1**: t_R 17.4 min; **2** t_R 17.5 min) was detected from **1** and **2**.

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