Two Diterpenes and Three Diterpene Glucosides from *Phlogacanthus curviflorus*

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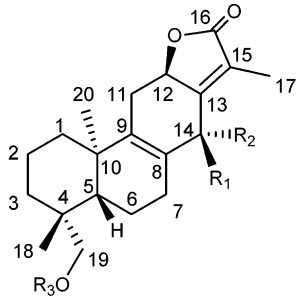
Two new diterpene lactones, phlogacantholides B (**1**) and C (**2**), and three new diterpene lactone glucosides, phlogacanthosides A (**3**), B (**4**), and C (**5**), together with lupeol, β-sitosterol, betulin, β-daucosterol, (+)-syringaresinol, and (+)-syringaresinol-4-*O*-β-D-glucopyranoside, were isolated from the roots of *Phlogacanthus curviflorus*. Their structures were elucidated by chemical and spectroscopic evidence. The structure, including the relative configuration of phlogacantholide B (**1**), was confirmed by X-ray crystallographic analysis of its diacetate (**6**).

Phlogacanthus curviflorus (Wall) Nees (Acanthaceae) is a shrub distributed in Yunnan Province of China as well as in Vietnam and India.[1] Its roots are used for the treatment of malaria.[2] Several diterpene lactones[3,4] and their glucosides,[5,6] steroids, and triterpenes[4] were isolated from some species of *Phlogacanthus*. However, there is no report about the chemical investigation on *P. curviflorus*.

In this study, five new compounds were isolated from the EtOH extract of the roots of *P. curviflorus*. On the basis of chemical and spectroscopic evidence, they were determined to be 14β,19-dihydroxyabieta-8,13(15)-dien-16,12-olide (phlogacantholide B, **1**), 14α,19-dihydroxyabieta-8,13(15)-dien-16,12-olide (phlogacantholide C, **2**), 14β,19-dihydroxyabieta-8,13(15)-dien-16,12-olide 19-*O*-β-D-glucopyranoside (phlogacanthoside A, **3**), 19-hydroxy-14-oxoabieta-8,13(15)-dien-16,12-olide 19-*O*-β-D-glucopyranoside (phlogacanthoside B, **4**), and 14β,19-dihydroxyabieta-8,13(15)-dien-16,12-olide 19-*O*-[2-(4-hydroxy-3,5-dimethoxybenzoyl)]-β-D-glucopyranoside (phlogacanthoside C, **5**) (Figure 1). The structure, including the relative configuration of phlogacantholide B (**1**), was confirmed by X-ray crystallographic analysis of its diacetate (**6**). The known compounds are betulin, β-sitosterol, β-daucosterol, lupeol,[7] (+)-syringaresinol, and (+)-syringaresinol-4-*O*-β-D-glucopyranoside.[8]

Compound **1** was isolated as colorless needles. Its molecular formula, $C_{20}H_{28}O_4$, was established from the quasi molecular ion peak at *m/z* 331.1917 $[M - H]^-$ in the HRESIMS spectrum. The IR absorptions at 1738 and 1678 cm^{-1} and the ^{13}C NMR signals at δ175.3, 162.9, and 120.7 (Table 1) revealed the presence of an α,β-unsaturated γ-lactone. The ^{13}C NMR spectrum showed 20 signals, of which three were for methyls (δ 9.5, 19.4, 27.7) and one for a hydroxymethyl group (δ 64.1), indicating an abietane diterpene with an α,β-unsaturated γ-lactone (Table 1). The major structure of **1** was elucidated by HMBC and NOESY experiments (Figure 1). To discriminate the lactonization between C-16 and C-12, and between C-16 and C-14, this compound was acetylated to give a diacetate (**6**). The HMBC correlation observed between H-14 (δ 6.36) and the carbonyl of the acetate (C-2′, δ 170.6) in **6**, formed from the acetylation at the 14-OH in **1**, suggested the lactonization in **6** between C-16 and C-12. The relative configuration of **1** was determined by NOESY experiments (Figure 1), in which H-14 and H-19 exhibited a NOE with H-20, and H-7α and H-12 exhibited NOEs with H-14, while H-5 exhibited a NOE with H-7β. Thus, the structure of **1** was determined as 14β,19-dihydroxyabieta-8,13(15)-dien-16,12-olide (phlogacantholide B). X-ray crystallographic analysis of phlogacantholide B diacetate (**6**) (Figure 2) confirmed the proposed structure and established the relative configuration.



1 R_1 = OH, R_2 = R_3 = H

2 R_1 = R_3 = H, R_2 = OH

3 R_1 = OH, R_2 = H, R_3 = β-*D*- glucopyranosyl

4 R_1 R_2 = O, R_3 = β-*D*- glucopyranosyl

5 R_1 = OH, R_2 = H,

R_3 = 2•-(4-hydroxy-3, 5-dimethoxybenzoyl)- β-*D*- glucopyranosyl

6 R_1 = OAc, R_2 = H, R_3 = Ac

7 R_1 = H, R_2 = OAc, R_3 = Ac

Compound **2** was isolated as colorless needles. The same molecular formula, $C_{20}H_{28}O_4$, as **1** was observed from the quasi molecular ion peak at *m/z* 331.1912 $[M - H]^-$ in the HRESIMS spectrum. The IR spectrum and NMR data (Table 1) were similar to those of **1** except for differences in ^1H NMR signals for H-7β, H-12, H-14, and H-17 and the ^{13}C NMR signals for C-9 and C-14. The NMR data of its acetylated product (**7**) were also similar to those of **6** except for differences in ^1H NMR signals of H-12, H-14, and H-17 and in ^{13}C NMR signals for C-9, C-14, and C-15. The ^1H NMR signal for H-14 shifted from δ 4.98 in **2** to δ 6.10 in **7**, which indicated that the acetyl group could be located at C-14 in **7**. Therefore, the lactonization between C-16 and C-12 was concluded. This conclusion was supported by the HMBC correlation between H-14 and the carbonyl of the C-14 acetate (C-2′, δ 170.4) in **7**. Thus, **2**

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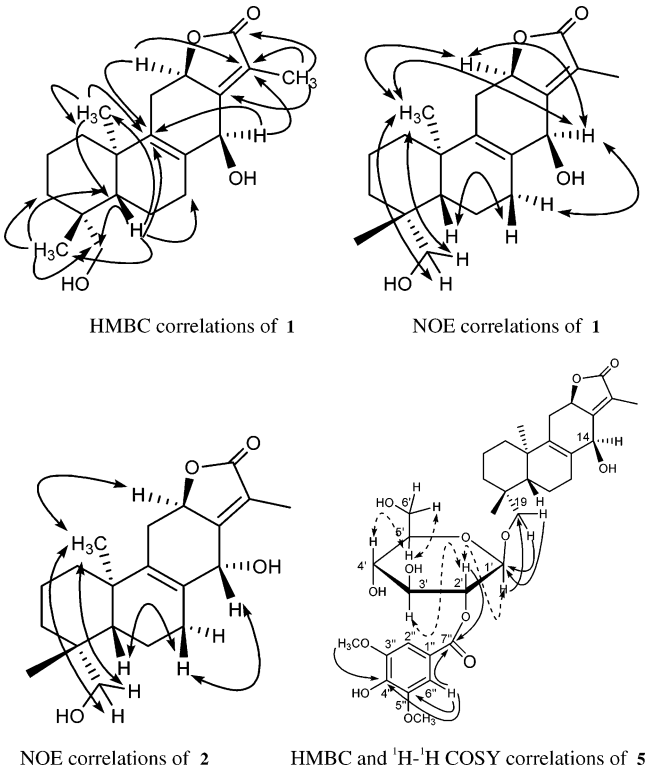

Figure 1. Important NMR correlations (HMBC: →; NOESY: ↔; ^{1}H−^{1}H COSY: <- - ->) of **1**, **2**, and **5**.

appeared to be a stereoisomer of **1**. This assumption was further supported by evidence obtained from the NOESY cross signal between H-14 and H-7β as well as the disappearance of correlations between H-14 and H-12, or H-20 (Figure 1). Consequently, the structure of **2** was elucidated as 14α,19-dihydroxyabieta-8,13(15)-dien-16,12-olide (phlogacantholide C).

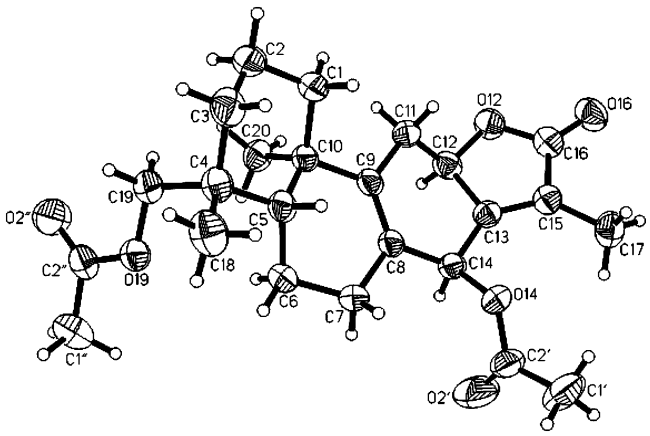

Figure 2. ORTEP diagram of **6**.

Compound **3** was isolated as colorless needles. Its molecular formula was determined to be $C_{26}H_{38}O_9$ on the basis of the ion peak at *m/z* 493.2438 [M − H]$^-$ in the HRESIMS spectrum. The IR spectrum suggested the presence of hydroxyl groups (3426 cm^{-1}) and an α,β-unsaturated γ-lactone (1738, 1683 cm^{-1}). Acid hydrolysis of **3** afforded D-glucose, which was detected by TLC and identified by its optical rotation. The ^{1}H NMR signal at δ 4.84 (d, 1H, J = 7.7 Hz) suggested a β-D-glucopyranoside. Besides the signals for the β-D-glucopyranosyl group, the close similarity of the ^{13}C NMR data to those of **1** suggested **3** was the glucoside of phlogacantholide B. The ^{13}C NMR signal for C-19 shifted from δ 64.1 in **1** to δ 74.4 in **3**, which indicated that the β-D-glucopyranosyl moiety could be located at C-19. Thus, **3** was elucidated as 14β,19-dihydroxyabieta-8,13(15)-dien-16,12-olide 19-*O*-β-D-glucopyranoside (phlogacanthoside A).

Compound **4** was isolated as colorless needles. Its molecular formula, $C_{26}H_{36}O_9$, was established from the quasi molecular ion peak at *m/z* 491.2272 [M − H]$^-$ in the HRESIMS spectrum. The IR peaks at 1767, 1756, and 1675

Table 1. ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) Data of **1**, **2**, **6**, and **7** in C_5D_5N[a]

	1		**2**		**6**		**7**	
position	δ_H (mult., Hz)	δ_C	δ_H (mult., Hz)	δ_C	δ_H (mult., Hz)	δ_C	δ_H (mult., Hz)	δ_C
1α	0.74 (m)	36.0	0.95 (m)	37.2	1.11 (m)	35.6	0.86 (m)	35.4
1β	1.52 (m)		1.62 (m)		1.74 (m)		1.53 (m)	
2α	1.33 (m)	18.7	1.40 (m)	20.0	1.50 (m)	18.4	1.34 (m)	18.5
2β	1.58 (m)		1.62 (m)		1.61 (m)		1.53 (m)	
3α	0.87 (m)	35.8	0.95 (m)	37.0	1.01 (m)	36.1	0.92 (m)	36.1
3β	2.10 (m)		2.14 (m)		1.71 (m)		1.67 (m)	
4		39.8		40.3		37.1		37.2
5	1.14 (d, 12.8)	52.3	1.27 (d, 12.7)	53.3	1.32 (d, 12.9)	52.0	1.10 (d, 12.9)	51.5
6α	1.58 (m)	19.0	1.62 (m)	20.3	1.52 (m)	18.5	1.44 (m)	18.8
6β	1.94 (m)		2.00 (m)		1.89 (m)		1.81 (m)	
7α	2.10 (m)	29.5	2.00 (m)	30.1	1.95 (m)	28.4	1.81 (m)	28.5
7β	2.74 (m)		3.05 (m)		2.05 (m)		2.34 (m)	
8		130.6		130.4		125.7		124.8
9		137.1		139.6		141.0		142.5
10		38.3		39.5		38.6		38.4
11β	1.83 (m)	33.3	1.88 (m)	34.7	1.95 (m)	32.7	1.81 (m)	33.5
11α	2.85 (m)		2.95 (m)		2.89 (m)		2.95 (m)	
12	4.86 (t, 8.4)	78.2	5.32 (t, 8.0)	77.9	4.73 (t, 8.1)	77.9	5.12 (t, 8.1)	76.4
13		162.9		163.5		156.2		155.8
14	5.16 (s)	69.9	4.98 (s)	64.9	6.36 (s)	70.4	6.10 (s)	66.8
15		120.7		121.6		121.3		124.7
16		175.3		176.4		174.3		174.5
17	2.34 (s)	9.5	1.94 (s)	9.8	1.83 (s)	8.7	2.13 (s)	9.3
18	1.16 (s)	27.7	1.23 (s)	28.9	0.99 (s)	27.4	0.99 (s)	27.2
19	3.67 (d, 10.8)	64.1	3.67 (d, 10.7)	65.2	3.91 (d, 11.1)	67.1	3.96 (d, 10.8)	66.1
	3.96 (d, 10.7)		3.98 (d, 10.7)		4.19 (d, 11.1)		4.35 (d, 11.0)	
20	1.00 (s)	19.4	0.98 (s)	20.8	1.03 (s)	19.6	0.92 (s)	19.3
1′[b]					2.20 (s)	20.8	2.07 (s)	20.7
2′[b]						170.6		170.4
1″[c]					2.05 (s)	21.2	2.05 (s)	20.7
2″[c]						171.5		170.9

[a] The assignments were based on ^{1}H−^{1}H COSY, HSQC, and HMBC experiments. [b] C atoms in 14-acetate. [c] C atoms in 19-acetate.

Table 2. ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) Data of **3**, **4**, and **5** in C_5D_5N[a]

	3		**4**		**5**	
position	δ_H (mult., Hz)	δ_C	δ_H (mult., Hz)	δ_C	δ_H (mult., Hz)	δ_C
1α	0.83 (m)	37.8	0.91 (m)	37.5	0.65 (m)	35.8
1*β*	1.48 (m)		1.65 (m)		1.44 (m)	
2α	1.27 (m)	19.9	1.35 (m)	19.6	1.21 (m)	18.8
2*β*	1.58 (m)		1.65 (m)		1.44 (m)	
3α	0.71 (m)	37.0	1.00 (dt, 13.1, 3.4)	36.3	0.81 (m)	37.7
3*β*	2.05 (m)		2.44 (d, 12.9)		1.44 (m)	
4		39.4		41.3		37.4
5	1.08 (d, 12.7)	53.5	1.09 (d, 12.1)	52.5	0.95 (d, 12.3)	52.3
6α	1.71 (m)	20.3	1.65 (m)	19.7	1.58 (m)	20.2
6*β*	1.92 (m)		1.96 (m)		1.87 (m)	
7α	1.92 (m)	30.6	1.91 (m)	29.1	1.55 (m)	29.7
8		131.9		135.1		131.2
9		138.0		152.6		136.0
10		39.2		39.3		38.5
11*β*	1.81 (m)	34.4	2.10 (m)	34.3	1.75 (m)	33.2
11α	2.82 (m)		3.14 (m)		2.79 (m)	
12	4.81 (t, 8.4)	79.9	5.17 (t, 8.4)	80.5	4.80 (t, 8.3)	78.1
13		164.0		163.2		163.0
14	5.11 (s)	71.1		186.5	5.01 (s)	69.8
15		121.8		131.1		120.5
16		176.4		174.9		175.2
17	2.32 (s)	10.6	2.24 (s)	11.0	2.21 (s)	9.4
18	1.16 (s)	29.2	1.18 (s)	26.8	0.99 (s)	28.4
19	3.64 (d, 9.6)	74.4	3.65 (d, 9.7)	74.5	3.78 (d, 10.1)	75.4
	4.27 (d, 9.7)		4.23 (m)		4.03 (d, 9.8)	
20	1.03 (s)	20.4	1.10 (s)	20.2	1.10 (s)	18.8
1′	4.84 (d, 7.7)	106.4	4.84 (d, 7.8)	106.4	5.09 (d, 8.0)	102.6
2′	4.04 (m)	76.5	4.04 (m)	76.4	5.92 (t, 8.8)	75.6
4′	4.23(m)	72.9	4.23 (m)	73.0	4.34 (t, 9.2)	71.9
5′	3.96 (m)	79.5	3.98 (m)	80.0	4.06 (m)	78.9
6′	4.56 (d, 11.6)	64.0	4.57 (dd, 11.6, 2.3)	64.0	4.60 (d, 11.8)	62.6
	4.39 (dd, 11.5, 5.2)		4.40 (dd, 11.8, 5.2)		4.41 (dd, 11.8, 5.2)	
1″						120.7
2″6″					7.75 (s)	108.6
3″5″						148.4
4″						142.5
7″						166.0
3″, 5″OCH$_3$					3.76 (s)	56.3

[a] The assignments were based on ^{1}H−^{1}H COSY, HSQC, and HMBC experiments.

cm^{-1} and the ^{13}C NMR signals at δ 186.5, 174.9, 163.2, and 131.1 (Table 2) revealed the presence of a carbonyl carbon and an α,*β*-unsaturated *γ*-lactone. Acid hydrolysis of **4** afforded D-glucose, which was identified by TLC and by its optical rotation. The ^{1}H NMR signal at H-1′ (δ4.84, d, J = 7.8 Hz) suggested a *β*-D-glucopyranosyl. The comparison of ^{13}C NMR data of **4** and **3** showed that the signal for C-14 was at δ 186.5 in **4** instead of at δ 71.1 as observed in **3**, indicating that C-14 in **4** was a carbonyl carbon. Thus, **4** was elucidated as 19-hydroxy-14-oxoabieta-8,13(15)-dien-16,12-olide 19-*O*-*β*-D-glucopyranoside (phlogacanthoside B).

Compound **5** was isolated as a white powder. The quasi molecular ion peak at *m/z* 673.2845 suggested the molecular formula $C_{35}H_{46}O_{13}$. The IR spectrum suggested the presence of an α,*β*-unsaturated *γ*-lactone (1738 cm^{-1}) and a phenyl group (1612, 1516, 1464 cm^{-1}). The ^{1}H NMR signal at δ 7.75 (2 H, s) and ^{13}C NMR signals at δ_C 148.4, 142.5, 120.7, and 108.6 indicated that **5** possessed a symmetrical tetrasubstituted phenyl group. From an HMBC experiment, this moiety was determined to be the 4-hydroxy-3,5-dimethoxybenzoyl group (Figure 1). Upon comparison of the ^{1}H NMR and ^{13}C NMR data of **5** with those of **3** (Table 2) (except the signals for the 4-hydroxy-3,5-dimethyoxybenzoyl), the close similarity of the ^{1}H NMR and ^{13}C NMR data indicated that **5** was an acylated product of **3**. From the ^{1}H−^{1}H COSY experiment (Figure 1) the ^{1}H NMR signal at δ 5.92 could be assigned to H-2′. The benzoyl moiety was located at C-2′ by the HMBC correlation between H-2′ (δ 5.92) and C-7″ (δ 166.0). From the HMBC correlations between H-1′and C-19 and between H-19 and C-1′, the glucosyl group was assigned to C-19. Compound **5** was therefore characterized as 14*β*,19-dihydroxyabieta-8,13(15)-dien-16,12-olide 19-*O*-[2-(4-hydroxy-3,5-dimethoxybenzoyl)]-*β*-D-glucopyranoside (phlogacanthoside C).

Experimental Section

General Experimental Procedures. Melting points were determined on an XRC-1 melting point apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer 341 automatic polarimeter. UV and IR spectra were measured on a Lambda 35 spectrometer and a Perkin-Elmer FT-IR spectrometer (KBr disk), respectively. Mass spectra were obtained on a Finnigan-LCQ^{DECA} mass spectrometer (ESI-MS) and an API Q-STAR Pulsar i mass spectrometer (HRESIMS). NMR spectra were recorded on a Bruker Avance 600 spectrometer with TMS as internal standard. Column chromatography (CC) was carried out on silica gel (200−300 mesh; Qingdao Haiyang Chemical Group Co. of China), and column fractions were monitored via thin-layer chromatography (TLC) over silica gel 60H (Qingdao Haiyang Chemical Group Co. of China) precoated plates. Resin adsorption chromatography was performed using macroporous resin D101 (The Chemical Plant of Nankai University, China).

Plant Material. Roots of *P. curviflorus* were collected in August 1999 at Xishuangbanna, Yunnan Province of China, and identified by Prof. Jing-Yun Cui at Xisuanbanna Tropic Botanic Garden, the Chinese Academy of Sciences. A voucher specimen (No. GF-38) was deposited in the Department for Natural Products Research at Chengdu Institute of Biology, the Chinese Academy of Sciences.

Extraction and Isolation. Air-dried and powdered roots of *P. curviflorus* (6.5 kg) were extracted with 95% EtOH (20 L × 4, each 7 days) at room temperature. After evaporating the

solvents in vacuo at 50 °C, a residue (350 g) was obtained. This residue was dissolved in H_2O (1 L) and then extracted successively with petroleum ether (60−90 °C, 1 L × 10), EtOAc (1 L × 5), and n-BuOH (1 L × 4) to afford corresponding fractions P (125 g), E (80 g), and B (114 g).

Fraction E was subjected to silica gel column chromatography (CC) and eluted gradiently with $CHCl_3$−MeOH (60:1 → 3:1) to give fractions E1−7. Fraction E2 (11.2 g) was separated by silica gel CC with petroleum ether (60−90 °C)−acetone (10:1) to give three subfractions, from which lupeol (1.5 g), β-sitosterol (0.4 g), and betulin (1.8 g) were obtained successively by recrystallization from acetone. **1** (0.9 g) was obtained from E3 (3.3 g) by recrystallization from MeOH. The remnant of E3 (2.3 g) was applied on silica gel CC, eluted with $CHCl_3$−acetone (5:1) to afford **2** (27 mg). β-Daucosterol (2.5 g) was obtained from E5 (13.1 g) by recrystallization from MeOH. E6 (18.7 g) was dissolved in 20 mL of MeOH, and then 20 mL of acetone was added to the precipitated white powder (4.9 g), which was then further subjected to silica gel CC, via elution with $CHCl_3$−MeOH (10:1), to afford **3** (280 mg) and **4** (3.2 g).

Fraction B was subjected to macroporous resin D101 CC eluted with H_2O, 70% EtOH, and 95% EtOH to give fractions B1−3. Fraction B2 (61 g) was divided into subfractions 1−5 by silica gel CC, eluted with $CHCl_3$−MeOH (20:1 → 1:1). **1** (2.5 g) was obtained from subfraction 1 (5.2 g) by recrystallization from MeOH, and the remnant (2.6 g) was then subjected to silica gel CC eluted with $CHCl_3$−EtOAc−MeOH (20:1:1) to afford (+)-syringaresinol (20 mg). **5** (5 mg) was isolated from subfraction 2 (11.3 g) by silica gel CC eluted with $CHCl_3$−acetone−MeOH (10:1:1). The separation of subfraction 4 (8.7 g) by silica gel CC eluted with $CHCl_3$−2-propanol−MeOH (10:1:1) afforded (+)-syringaresinol-4-*O*-β-D-glucopyranoside (70 mg) and **3** (270 mg).

Diacetylation of 1 and 2. Phlogacantholide B (**1**, 100 mg), C_5H_5N (1 mL), and Ac_2O (2 mL) were stirred at 20 °C for 12 h, and phlogacantholide B diacetate (**6**) (120 mg) was obtained by evaporation in vacuo. Phlogacantholide C (**2**, 3 mg), C_5H_5N (0.5 mL), and Ac_2O (1 mL) were similarly acetylated to yield 3 mg of phlogacantholide C diacetate (**7**).

X-ray Crystallography of 6. Phlogacantholide B diacetate (**6**, 60 mg) was dissolved in 0.5 mL of acetone. The solution was left for a week to give suitable crystals (55 mg). Crystal data: $C_{24}H_{32}O_6$; $M_r = 416.50$; dimensions 0.58 × 0.56 × 0.52 mm; orthorhombic, space group $P2_12_12_1$, $a = 7.806(1)$ Å, $b = 15.010(3)$ Å, $c = 18.893(3)$ Å, $\alpha = \beta = \gamma = 90°$, $V = 2213.7(5)$ Å^3, $Z = 4$, $D_{calc} = 1.250$ g/cm^3, $\lambda = 0.71073$ Å, μ(Mo Kα) = 0.089 mm^{-1}, $F(000) = 896$, $T = 296(2)$ K. Of the 3371 reflections collected, 3035 was unique ($R_{int} = 0.0064$). The structure was solved by direct methods with SHELX 97[10] and refined by full-matrix least-squares on F^2. Final refinement: data/restraints/parameters = 3035/0/277; R1 = 0.0561 (all data), wR2 = 0.0892 (all data); the Flack absolute structure parameter = 0(10), and GOF = 0.879. The H coordinates were determined by calculated geometry. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.144 and −0.129 e$^-$/Å^3, respectively. CCDC 235991 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK, fax: +44 1223 336033.

Acid Hydrolysis of 3 and 4. Phlogacanthoside A (**3**, 20 mg) was heated with 2 mL of 2.5 mol/L HCl at 70 °C for 3 h. After 5 mL of H_2O was added and the mixture was extracted with EtOAc, the aqueous phase was evaporated in vacuo to yield 7 mg of D-glucose, which was detected by TLC and optical rotation $[\alpha]_D^{20}$ +51.8° (*c* 0.14, H_2O). Phlogacanthoside B (**4**, 20 mg) was treated as above to give 7 mg of D-glucose with an optical rotation $[\alpha]_D^{20}$ +54.1° (*c* 0.12, H_2O).

Phlogacantholide B (1): colorless needles (MeOH); mp 211−213 °C; $[\alpha]_D^{25}$ −223.6°, $[\alpha]_{578}^{25}$ −237.3°, $[\alpha]_{546}^{25}$ −273.6°, $[\alpha]_{436}^{25}$ −493.6°, $[\alpha]_{365}^{25}$ −840.9° (*c* 0.11, MeOH); $R_f = 0.38$ ($CHCl_3$−acetone, 5:1); UV (MeOH) λ_{max} (log ϵ) 224 (3.64) nm; IR (KBr) ν_{max} 3436, 2930, 1738, 1678, 1086, 1057, 1023, 1013 cm^{-1}; ^{1}H NMR and ^{13}C NMR data, see Table 1; ESIMS (negative mode) *m/z* 331 [M − H]$^-$ (100), 663 [2M − H]$^-$ (18); HRESIMS (negative ion) *m/z* 331.1917 (calcd for $C_{20}H_{27}O_4$ [M − H]$^-$, 331.1909).

Phlogacantholide C (2): colorless needles (acetone); mp 181−183 °C; $[\alpha]_D^{25}$ −253.6°, $[\alpha]_{578}^{25}$ −279.1°, $[\alpha]_{546}^{25}$ −321.8°, $[\alpha]_{436}^{25}$ −592.7°, $[\alpha]_{365}^{25}$ −1035° (*c* 0.11, MeOH); $R_f = 0.20$ ($CHCl_3$−acetone, 5:1); UV (MeOH) λ_{max} (log ϵ) 223 (3.40) nm; IR (KBr) ν_{max} 3400, 2926, 1737, 1689, 1637, 1043, 1019 cm^{-1}; ^{1}H NMR and ^{13}C NMR data, see Table 1; ESIMS (negative mode) *m/z* 331 [M − H]$^-$ (100), 663 [2M − H]$^-$ (16); HRESIMS (negative ion) *m/z* 331.1912 (calcd for $C_{20}H_{27}O_4$ [M − H]$^-$, 331.1909).

Phlogacanthoside A (3): colorless needles (MeOH); mp 148−149 °C (MeOH); $[\alpha]_D^{25}$ −264.7° (*c* 0.15, MeOH); UV (MeOH) λ_{max} (log ϵ) 222 (4.39) nm; IR (KBr) ν_{max} 3426, 2929, 1738, 1683, 1647, 1076, 1036, 1017 cm^{-1}; ^{1}H NMR and ^{13}C NMR data, see Table 2; ESIMS (negative mode) *m/z* 493 [M − H]$^-$ (78), 987 [2M − H]$^-$ (100); HRESIMS (negative ion) *m/z* 493.2438 (calcd for $C_{26}H_{37}O_9$ [M − H]$^-$, 493.2437).

Phlogacanthoside B (4): colorless needles (MeOH); mp 136−137 °C (MeOH); $[\alpha]_D^{25}$ −109.4° (*c* 0.16, MeOH); UV (MeOH) λ_{max} (log ϵ) 288 (4.37), 219 (4.0) nm; IR (KBr) ν_{max} 3401, 2927, 1767, 1756, 1675, 1640, 1078, 1038, 1016 cm^{-1}; ^{1}H NMR and ^{13}C NMR data, see Table 2; ESIMS (negative mode) *m/z* 491 [M − H]$^-$ (100), 983 [2M − H]$^-$ (98); HRESIMS (negative ion) *m/z* 491.2272 (calcd for $C_{26}H_{35}O_9$ [M − H]$^-$, 491.2281).

Phlogacanthoside C (5): white powder; $[\alpha]_D^{25}$ −137.1° (*c* 0.14, MeOH); UV (MeOH) λ_{max} (log ϵ) 218 (4.493) nm; IR (KBr) ν_{max} 3436, 2929, 2850, 1738, 1612, 1516, 1464, 1424, 1337, 1224, 1117, 1076, 1028, 1018, 990, 761 cm^{-1}; ^{1}H NMR and ^{13}C NMR data, see Table 2; ESIMS (negative mode) *m/z* 673 [M − H]$^-$ (100); HRESIMS (negative ion) *m/z* 673.2845 (calcd for $C_{35}H_{45}O_{13}$ [M − H]$^-$, 673.2860).

Phlogacantholide B diacetate (6): colorless needles (acetone); mp 181−182 °C; $[\alpha]_D^{25}$ −210.7° (*c* 0.15, MeOH); UV (MeOH) λ_{max} (log ϵ) 220 (4.31) nm; IR (KBr) ν_{max} 2930, 1756, 1725, 1692, 1252, 1227, 1067, 1028 cm^{-1}; ^{1}H NMR and ^{13}C NMR data, see Table 1; ESIMS (positive mode) *m/z* 417 [M + H]$^+$ (90), 439 [M + Na]$^+$ (31), 455 [M + K]$^+$ (11).

Phlogacantholide C diacetate (7): white powder; $[\alpha]_D^{25}$ −151.3° (*c* 0.08, MeOH); UV (MeOH) λ_{max} (log ϵ) 217 (3.88) nm; IR (KBr) ν_{max} 3436, 2924, 2869, 2852, 1771, 1746, 1631, 1371, 1245, 1226, 1029 cm^{-1}; ^{1}H NMR and ^{13}C NMR data, see Table 1; ESIMS *m/z* (negative mode) 415 [M − H]$^-$ (32).

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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