Rearranged Prenylated C_6-C_3 Compounds and a Highly Oxygenated *seco*-Prezizaane-Type Sesquiterpene from the Stem Bark of *Illicium oligandrum*

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Received March 14, 2009

Three new rearranged prenylated C_6-C_3 compounds, named illioliganones A, B, and C (**1**−**3**), and a new highly oxygenated *seco*-prezizaane-type sesquiterpene, oligandriortholactone (**7**), together with three known prenylated C_6-C_3 compounds (**4**−**6**) and a known sesquiterpene lactone (**8**), have been isolated from the stem bark of *Illicium oligandrum*. The structures of **1**−**3** and **7** were elucidated by spectroscopic methods including 1D and 2D NMR, HRMS, and CD experiments. The absolute configuration of the 11,12-diol moiety in **2** and **3** was determined on the basis of observing the induced circular dichroism after addition of $Mo_2(OAc)_4$ in DMSO solution. The anti-inflammatory and cytotoxic activities of **1**−**8** were evaluated.

The genus *Illicium* is a rich source of prenylated C_6-C_3 compounds, neolignans, and sesquiterpene lactones.[1] Prenylated C_6-C_3 compounds, also named phytoquinoids, are considered to be characteristic constituents, some of which are found to increase choline acetyltransferase activity.[2] From a chemical point of view, this type of compound contains C_6-C_3 and isoprene (C_5). *Illicium oligandrum* is a toxic shrub of this genus, mainly distributed in Southern China and used in folk medicine for treating rheumatoid arthritis. In the previous paper, a new sesquiterpene lactone and three new neolignan glycosides with antioxidant and anti-inflammatory activities were isolated from the fruits of the plant.[3] As part of our continuing search for novel bioactive constituents, the ethanol extract from the stem bark of *I. oligandrum* was investigated. As a result, three new rearranged prenylated C_6-C_3 compounds, illioliganones A (**1**), B (**2**), and C (**3**), together with three known prenylated C_6-C_3 compounds, 2,3-dehydroillifunone (**4**), illifunone C (**5**), and illifunone D (**6**), a new highly oxygenated *seco*-prezizaane-type sesquiterpene, named oligandriortholactone (**7**), and a known sesquiterpene, neomajucin (**8**), were isolated from the $CHCl_3$-soluble fraction of the ethanol extract. In this paper, we report the isolation and structure elucidation of new compounds and the determination of the absolute configurations of the *sec*/*tert vic*-diol moieties in **2** and **3** by using the in situ dimolybdenum CD method (Snatzke's method). The preliminary evaluation of anti-inflammatory activities and cytotoxicities of compounds **1**−**8** is also reported.

Results and Discussion

The $CHCl_3$ fraction of the ethanolic extract was subjected to column chromatography on Si gel, Sephadex LH-20, ODS, and HPLC to afford three new rearranged prenylated C_6-C_3 compounds (**1**−**3**) and a new highly oxygenated *seco*-prezizaane-type sesquiterpene (**7**), along with the known 2,3-dehydroillifunone (**4**),[4] illifunone C (**5**),[2a] illifunone D (**6**),[2a] and neomajucin (**8**),[5] by comparing with corresponding literature data.

Compound **1** was isolated as a colorless oil with the molecular formula $C_{14}H_{18}O_4$ established by positive HRESIMS (m/z = 273.1100 $[M + Na]^+$, calcd for 273.1097). Its IR spectrum revealed the presence of hydroxy (3448 cm^{-1}) and two carbonyl groups, including a saturated ketone (1744 cm^{-1}) and an α,β-conjugated ketone moiety (1672 cm^{-1}). The ^1H NMR spectrum of **1** showed resonances due to the β-H of an α,β-conjugated ketone moiety at δ_H 6.80 (1 H, s, H-3), two hydroxy group protons at δ_H 5.01 (1H, s, HO-4) and 4.14 (1 H, d, J = 5.6 Hz, HO-11), which could be exchanged by D_2O, an isolated methine proton at δ_H 3.04 (1 H, s, H-6), and two methyl groups at δ_H 1.02 (3 H, s, CH_3-13) and 0.91 (3 H, s, CH_3-14). The presence of *gem*-dimethyl (CH_3-13, -14) groups linked to a quaternary carbon at δ_C 44.3 (C-12) was determined by HMBC experiments. In addition, the NMR data also indicated the presence of an allyl group [δ_H 2.97 (2 H, m, H-7), 5.83 (1 H, m, H-8), 5.03 (1 H, d, J = 10.4 Hz, H-9a), 5.11 (1 H, d, J = 17.2 Hz, H-9b); δ_C 33.2 (C-7), 135.5 (C-8), 117.5 (C-9)] and a unit comprising CH_2(10)−CH(11)−OH [δ 1.94 (1 H, dd, J = 12.4, 12.4 Hz, H-10α), 2.23 (1 H, dd, J = 12.4, 5.2 Hz, H-10β), 3.56 (1 H, ddd, J = 11.2, 5.6, 5.2 Hz, H-11); δ 42.2 (C-10), 71.2 (C-11)], which were verified by $^1H-^1H$ COSY, HMQC, and HMBC experiments. In the HMBC experiment, the long-range correlations from H-11 to C-12, C-6, and C-4, from H-6 to C-11, C-12, C-5, and C-4, and from H_2-10 to C-4 and C-5 confirmed that **1** possesses a cyclohexanone ring. HMBC correlations from H-6 to the α,β-conjugated carbonyl (δ_C 195.4, C-1) and C-2 (δ_C 140.1) and from the β-H (H-3) of the α,β-conjugated ketone moiety to the saturated carbonyl (δ_C 204.4, C-5), C-4 (δ_C 77.7), and C-10 (δ_C 42.2) indicated unambiguously that the carbonyl and β-carbon of the α,β-conjugated ketone unit were connected with the cyclohexanone ring at C-6 and C-4, respectively. HMBC correlations between H-8 and C-2 and between H-3 and C-7 established that the allyl group was attached to C-2 of the α,β-conjugated ketone unit. On the basis of the above spectroscopic analysis, the gross structure of **1** was established as shown in Figure 1.

The absolute configuration of **1** was established from its CD Cotton effects. Compound **1** showed a negative Cotton effect at 336 nm for the n→ π^* excitation, a negative Cotton effect at 261 nm, and a positive Cotton effect at 231 nm for the $\pi \rightarrow \pi^*$ excitation of the α,β-conjugated ketone chromophore, which were similar to those of denudadione A[6] and contrary to those of liliflodione.[7] Therefore, the absolute configurations for C-4 and C-6 were determined to be both *R*. In addition, the double doublet signal at δ_H 3.56 for H-11 in the ^1H NMR spectrum in $CDCl_3$ with a large and a small coupling constant (J = 11.2, 5.2 Hz) indicated the β-orientation of H-11; thus, the absolute configuration for C-11 was also *R*. Accordingly, the structure of illioliganone A (**1**) was elucidated as shown in Figure 1.

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10.1021/np9001702 CCC: $40.75
Published on Web 06/04/2009

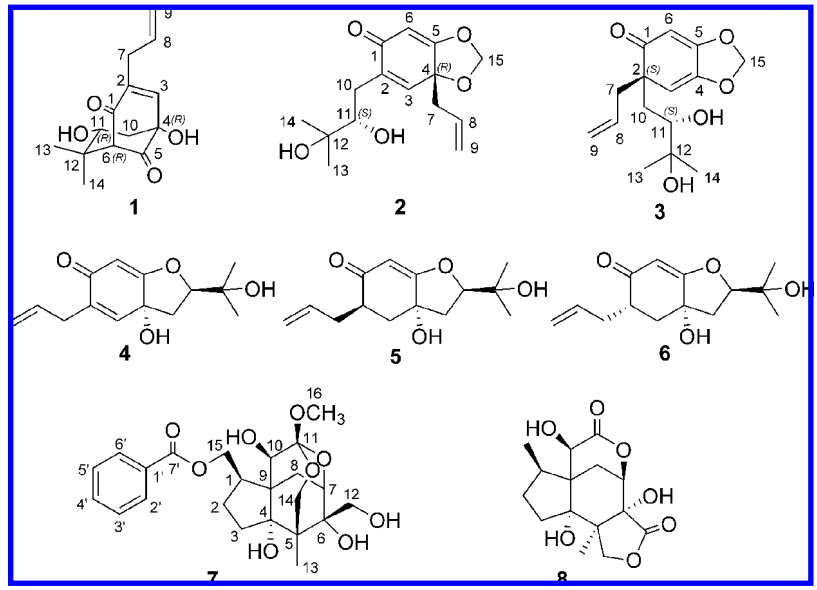

Figure 1. Structures of compounds **1**−**8**.

Compound **2** was obtained as a colorless oil. Its molecular formula of $C_{15}H_{20}O_5$ was determined by HRESIMS (m/z = 281.1388 $[M + H]^+$, calcd for 281.1383). Its IR spectra displayed absorption bands attributable to a hydroxy group (3422 cm^{-1}) and a dienone moiety (1675, 1615 cm^{-1}). The presence of the dienone group in **2** was also indicated by the UV absorption maxima at 245 and 295 nm. The NMR data of **2** revealed two singlets at δ_H 5.41 and 6.89 due to the α- and β'-protons (H-6 and H-3) of the dienone moiety, two exchangeable hydroxy protons at δ_H 3.53 (1 H, d, J = 5.0 Hz, HO-11) and 3.38 (1 H, s, HO-12), an allylic group [δ_H 5.79 (1 H, m• H-8), 5.14 (1 H, dd, J = 17.0, 2.0 Hz, H-9a), 5.10 (1 H, dd, J = 10.0, 2.0 Hz, H-9b), 2.73 (1 H, dd, J = 13.5, 7.5 Hz, H-7a), 2.49 (1 H, dd, J = 13.5, 7.5 Hz, H-7b)], a methylenedioxy group [δ_H 5.70, 5.72 (each 1 H, s, H_2-15); δ_C 98.8 (C-15)], and a dimethylcarbinol group [δ_H 1.17 (3 H, s, CH_3-13), 1.16 (3 H, s, CH_3-14); δ_C 25.9 (C-13), 25.3 (C-14), 72.8 (C-12)]. The ^1H and ^{13}C NMR data also showed the presence of a CH_2(10)−CH(11)−OH unit [δ_H 2.72 (1 H, d, J = 14.0 Hz, H-10a), 2.10 (1 H, dd, J = 14.0, 10.0 Hz, H-10b), 3.46 (1 H, br d, J = 10.0 Hz, H-11); δ_C 32.8 (C-10), 77.5 (C-11)], which was confirmed by HMQC and HMBC experiments. Both the methyl signals (CH_3-13 and CH_3-14) showed three-bond correlations with C-11 in the HMBC spectrum; therefore, the dimethylcarbinol group was bonded to C-11 and gave rise to a 2,3-dihydroxy-3-methylbutyl group as a C_5 unit. The above spectroscopic data of **2** exhibited the typical feature of prenylated C_6−C_3 compounds isolated from some species of the genus *Illicium* and were similar to those of illicinone C except for the data of the C_5 unit.[2a] Moreover, in the HMBC spectrum, long-range correlations of H_2-10/C-1 (C═O), H_2-10/C-2, H_2-10/C-3, and H-11/C-2 indicated that the 2,3-dihydroxy-3-methylbutyl group was linked to C-2. The attachment between the allyl group and C-4 was unequivocally verified by the long-range correlations between H_2-7 and C-3, C-4, and C-5. Thus, the locations of the allyl and the 2,3-dihydroxy-3- methylbutyl groups were contrary to those in illicinone C.[2a] The absolute configuration of C-4 was determined to be *R* on the basis of the CD positive Cotton effect at 280 nm resulting from the n → π* excitation of the α,β-conjugated ketone chromophore, which was contrary to that of illicinone G.[4]

The absolute configuration of the 11,12-diol moiety was determined by the in situ dimolybdenum CD method, developed by Snatzke and Frelek.[8−12] This practical, versatile, and reliable method involves the in situ formation of a metal complex of chiral *vic*-diol (cyclic and acyclic 1,2-diols) with the achiral dimolybdenum tetracetate [$Mo_2(OAc)_4$] acting as an auxiliary chromophore.

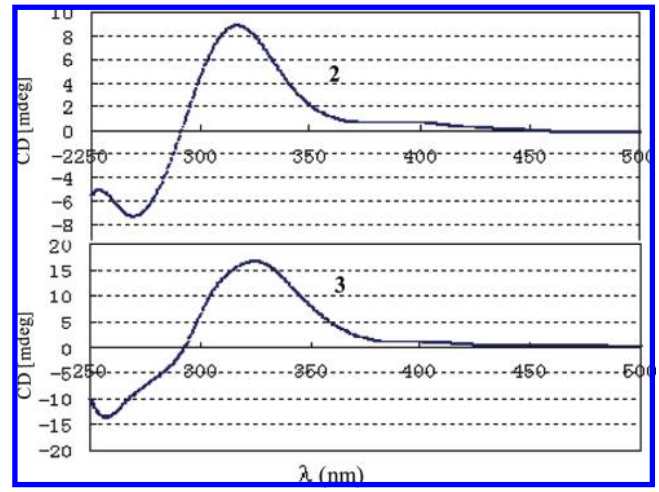

Figure 2. Circular dichroism spectra of **2** and **3** in DMSO solution of dimolybdenum tetracetate (the inherent CD spectra of **2** and **3** were subtracted).

The observed sign of the Cotton effects in the induced CD spectra depends solely on the chirality of the 1,2-diol moiety expressed by the sign of the O−C−C−O torsion angle. Thus, the absolute configuration of a *vic*-diol can be determined by means of the empirical helicity rule relating the Cotton effect sign of the diagnostic band at 310 nm with the helicity of the O−C−C−O subunit. As mentioned, compound **2** has an inherent CD resulting from the conjugated ketone chromophore. To avoid overlap of the inherent Cotton effects above 250 nm with those generated after addition of $Mo_2(OAc)_4$, the inherent CD contribution was subtracted to give the induced CD of the metal complex. Thus, the positive Cotton effect at 310 nm observed in the induced CD spectrum, as shown in Figure 2, permitted assignment of the *S*-configuration to C-11 on the basis of the empirical rule proposed by Snatzke. Therefore, the structure of illioliganone B (**2**) was elucidated as shown in Figure 1.

Compound **3** was obtained as a colorless oil. Its molecular formula, $C_{15}H_{20}O_5$, was determined by HRESIMS (m/z = 281.1385 $[M + H]^+$, calcd for 281.1383). Its IR spectrum displayed absorption bands attributable to a hydroxy (3391 cm^{-1}) and a conjugated ketone (1650, 1612 cm^{-1}) group. As in compound **2**, two singlets at δ 5.54 (H-3) and 5.46 (H-6) for two olefinic protons,

Table 1. ^{13}C and ^{1}H NMR Data of Compounds **1**, **2**, and **3** in Acetone-d_6[a]

	1		**2**		**3**	
position	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)	δ_C	δ_H (J in Hz)
1	195.4 s		187.8 s		202.1 s	
2	140.1 s		139.4 s		52.3 s	
3	149.4 d	6.80, s	136.9 d	6.89, s	108.3 d	5.54, s
4	77.7 s		81.8 s		145.1 s	
5	204.4 s		174.5 s		163.8 s	
6	73.7 d	3.04, s	98.3 d	5.41, s	99.6 d	5.46, s
7	33.2 t	2.97, m	40.6 t	2.73, dd (13.5, 7.5)	46.9 t	2.48, dd (13.2, 7.2)
				2.49, dd (13.5, 7.5)		2.24, dd (13.2, 7.2)
8	135.5 d	5.83, m	131.9 d	5.79, m	134.2 d	5.57, m
9	117.5 t	5.03, d (10.4)	120.5 t	5.14, dd (17.0, 2.0)	117.9 t	4.96, dd (16.8, 2.0)
		5.11, d (17.2)		5.10, dd (10.0, 2.0)		4.91, dd (10.0, 2.0)
10	42.2 t	Hα 1.94, dd (12.4, 12.4)	32.8 t	2.72, d (14.0)	43.3 t	2.10, d (13.6)
		Hβ 2.23, dd (12.4, 5.2)		2.10, dd (14.0, 10.0)		1.82, dd (13.6, 2.0)
11	71.2 d	3.56, ddd (11.2, 5.6, 5.2)	77.5 d	3.46, br. d (10.0)	76.3 d	3.33, m
12	44.3 s		72.8 s		72.6 s	
13	25.1 q	1.02, s	25.9 q	1.17, s	25.7 q	1.07, s
14	19.1 q	0.91, s	25.3 q	1.16, s	25.4 q	1.07, s
15			98.8 t	5.72, s; 5.70, s	102.3 t	5.89, s; 5.88, s
4-OH		5.01, s				
11-OH		4.14, d (5.6)		3.53, d (5.0)		3.05, d (6.0)
12-OH				3.38, s		3.27, s

[a] NMR data (δ) were measured at 400 MHz for proton and 100 MHz for carbon. The assignments were based on HMQC and HMBC experiments.

two exchangeable OH signals at δ 3.05 (1 H, d, J = 6.0 Hz, HO-11) and 3.27 (1 H, s, HO-12), and signals corresponding to an allyl group, a methylenedioxy group, and a 2,3-dihydroxy-3-methylbutyl group were evident in the ^{1}H and ^{13}C NMR data (Table 1) of **3**. This suggested that **3** possessed the same functional groups as **2** except for the C_6 unit of cyclohexadienone moiety. HMBC correlations from H-3 to C-1 (C=O), C-2, C-4, and C-5, from H-6 to C-1 (C=O), C-4, and C-5, and from H_2-15 to C-4 and C-5 indicated the presence of a cyclohexa-2,4-dienone ring (the C_6 unit), fused with the methylenedioxy group at C-4 and C-5 in **3**. In addition, both H_2-7 and H_2-10 exhibited three-bond correlations with the conjugated carbonyl (C-1) and C-3 (δ_C 108.3) in the HMBC experiments, suggesting that the allyl and the 2,3-dihydroxy-3-methylbutyl groups were all attached to C-2 of the cyclohexadienone ring. The absolute *S*-configuration for C-2 of **3** was established by the CD data, showing the same negative Cotton effect at 325 nm resulting from the n $\rightarrow \pi^*$ excitation of the cyclohexdienone ring as that at 328 nm of (−)-usnic acid.[13] The *S*-configuration for C-11 in **3** was determined by the dimolybdenum CD method as for **2**. Thus, the structure of illioliganone C (**3**) was elucidated as shown in Figure 1.

Compound **7** was isolated as a white powder. Its molecular formula, $C_{23}H_{30}O_9$, was established by HRESIMS (*m/z* 473.1772 $[M + Na]^+$), and the IR spectrum revealed the presence of hydroxy (3408 cm^{-1}) and ester carbonyl (1709 cm^{-1}) groups. A benzoyl and an O-methyl group were observed in the ^{1}H and ^{13}C NMR spectra (Table 2). Except for these groups, another 15 carbon signals were resolved in the ^{13}C NMR spectrum and categorized by DEPT experiments as one tertiary methyl (δ_C 15.8, CH_3-13), three methylene (CH_2-2, CH_2-3, CH_2-8), three oxygenated methylene (CH_2-12, CH_2-14, CH_2-15), three methine including two oxygenated methine (CH-1, O-CH-7, and O-CH-10), and five quaternary carbons at δ_C 89.2 (C-4), 47.3 (C-5), 79.1 (C-6), 49.8 (C-9), and 113.2 (C-11). Among these 15 carbon signals, no carbonyl signals were evident; C-11 (δ_C 113.2) could only be an sp^3 carbon substituted by three oxygen atoms, thus constituting an orthocarboxylic acid diester (ortholactone) group. In the $^{1}H-^{1}H$ COSY spectrum, correlations from H_2-15−H_2-2 to H_2-3 and from H-7 to H_2-8 indicated unambiguously the presence of CH_2(15)−CH(1)−CH_2(2)−CH_2(3) and CH_2(8)−CH(7) units. The above feature suggested that **7** belonged to the cycloparvifloralone subtype of *seco*-prezizaane-type sesquiterpenes.[14] Comparison of the NMR data of **7** with those of (11)7,14-ortholactone-3α-hydroxyfloridanolide, a similar compound isolated from *Illicium merrillianum*,[15]

Table 2. ^{13}C and ^{1}H NMR Data of Compound **7** in Acetone-d_6[a]

position	δ_C	δ_H (J in Hz)
1	44.6 d	2.69, m
2	26.3 t	Hα 1.53, m
		Hβ 1.97, m
3	31.6 t	Hα 2.38, m
		Hβ 1.53, m
4	89.2 s	
5	47.3 s	
6	79.1 s	
7	72.7 d	3.91, d (2.8)
8	32.6 t	Hα 1.90, dd (13.6, 2.8)
		Hβ 2.41, dd (13.6, 2.8)
9	49.8 s	
10	75.6 d	3.93, s
11	113.2 s	
12	73.2 t	3.60, d (9.2); 3.95, d (9.2)
13	15.8 q	1.09, s
14	67.1 t	4.17, d (12.5); 3.31, d (12.5)
15	66.7 t	4.52, d (7.2)
OCH_3	59.4 q	3.33, s
4-OH		5.05, s
6-OH		4.87, s
1′	131.4 s	
2′, 6′	130.1 d	8.03, d (7.6)
3′, 5′	129.4 d	7.51, dd (7.6, 7.6)
4′	133.7 d	7.62, dd (7.6, 7.6)
7′	166.7 d	

[a] NMR data (δ) were measured at 400 MHz for proton and 100 MHz for carbon. The assignments were based on HMQC and HMBC experiments.

indicated that C-12 and C-15 in **7** were both oxygenated methylene carbons. In the HMBC spectrum, the correlation between H_2-15 (δ_H 4.52, d, J = 7.2 Hz) and C-7′ (ester carbonyl, δ_C 166.7) indicated the benzoyloxy group was connected to C-15 by an ester bond. The only methoxy group was attached to C-11 on the basis of the HMBC correlation between H_3-16 (δ_H 3.33, s) and C-11 (δ_C 113.2) (Figure 3).

In addition, the relative configuration of **7** was deduced from the NOESY experiment (Figure 3). CH_2-12, CH_2-15, and HO-10 were all β-oriented, which were confirmed by the cross-peaks from H_2-12 to H-14b, from H_2-15 to H-10α, and from H-8β to H-10α. According to the above analysis, the structure of oligandriortholactone (**7**) was elucidated as shown in Figure 1.

The anti-inflammatory and cytotoxic activities of compounds **1**−**8** were evaluated. The anti-inflammatory activities of compounds

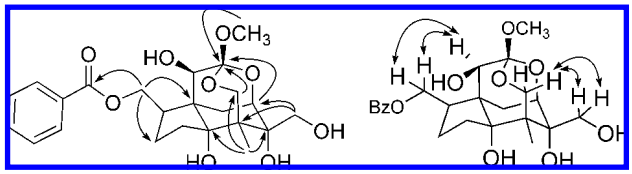

Figure 3. Key HMBC and NOESY correlations of **7**.

1−**8** were assessed by measuring the inhibitory ratios of β-glucuronidase[7] release in rat polymorphonuclear leukocytes (PMNs) induced by the platelet-activating factor (PAF) in vitro,[16] and the inhibitory ratios were −7.7, 33.8, 20.1, 4.8, −9.4, 18.0, 15.8, and 22.4% at a concentration of 10 μM. Ginkgolide B was used as a positive control, with an inhibitory ratio of 80.5% at 10 μM. These suggested that compounds **2**, **3**, and **6**−**8** showed weak inhibitory activities of β-glucuronidase release from rat PMNs induced by PAF. In addition, all tested compounds were not cytotoxic to HCT-8, Bel-7402, BGC-823, A549, and A2780 human tumoral cell lines.

Experimental Section

General Experimental Procedures. Melting point was determined on an XT-4 micro melting point apparatus (uncorrected). Optical rotations were measured on a Perkin-Elmer 341 digital polarimeter at 589 nm. UV spectra were recorded on a Hitachi UV-240 spectrophotometer. CD spectra were measured on a JASCO J-810 spectropolarimeter with a 0.1 cm cell at room temperature at the following conditions: speed 200 nm/min, time constant 1 s, bandwidth 2.0 nm. IR spectra were recorded as KBr disks on a Nicolet Impact 410 FT-IR spectrophotometer. NMR spectra were obtained on Inova 400 MHz spectrometers. ESIMS were measured on an Agilent 1100 Series LC/MSD trap mass spectrometer. HRESIMS were measured on a Bruker FTMS APEXIII 7.0T mass spectrometer. Column chromatography was performed on Si gel (200−300 mesh, Qingdao Marine Chemical Factory, China), ODS (40−70 μm, Merck), and Sephadex LH-20 (Amersham Pharmacia Biotech AB, Sweden). HPLC was carried out on a Shimadzu LC-6AD with an SPD-10A detector. A reversed-phase C18 column (YMC Pack ODS-A 20 × 250 mm, 10 μm) was employed. TLC was carried out with glass precoated Si gel GF_{254} plates (Qingdao Marine Chemical Factory, China). Spots were visualized under UV light or by spraying with 10% H_2SO_4 in 95% EtOH followed by heating.

Plant Material. The stem bark of *Illicium oligandrum* was collected from Guangxi Province, China, in September 2004, and identified by Prof. Song-ji Wei of Guang Xi Traditional Medical College. A voucher specimen (No. 04086) is deposited in the herbarium of the Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College.

Extraction and Isolation. The stem bark of *I. oligandrum* (3.0 kg) was air-dried, ground, and extracted three times (2 h for each time) with 95% EtOH (30 L) under reflux conditions (90−95 °C). The EtOH extract was evaporated to almost dryness in vacuo, and the resulting mixture (540 g) was suspended in H_2O and partitioned successively with petroleum ether (3.0 L), $CHCl_3$ (5.0 L), EtOAc (5.0 L), and *n*-BuOH (5.0 L). The $CHCl_3$ part (70 g) was subjected to Si gel column chromatography, eluted with petroleum ether/$(Me)_2CO$ (40:1, 20:1, 10:1, 5:1, 1:1, v/v) and $(Me)_2CO$, to yield fractions A_1−A_6. Fraction A_2 (18.0 g) was chromatographed on a Si gel column again with petroleum ether/EtOAc (5:1) and yielded **4** (3.8 g). Fraction A_3 (10.2 g) was subjected to Sephadex LH-20 column chromatography eluting with MeOH to give fractions A_3B_1 (2.0 g), A_3B_2 (4.8 g), and A_3B_3 (2.5 g). Fraction A_3B_2 was chromatographed on an ODS column with MeOH/H_2O (35:65) to yield **1** (52 mg) and **8** (10 mg). Fraction A_3B_3 was chromatographed on an ODS column with MeOH/H_2O (40:60), then purified by HPLC with MeOH/H_2O (48:52), to yield **2** (47 mg, t_R = 38.6 min). Fraction A_4 (8.5 g) was subjected to Sephadex LH-20 column chromatography eluting with MeOH and gave fractions A_4C_1 (0.8 g), A_4C_2 (1.2 g), A_4C_3 (3.5 g), and A_4C_4 (2.8 g). Fraction A_4C_2 was purified by HPLC with MeOH/H_2O (38:62) to yield **7** (35 mg, t_R = 43.2 min). Fraction A_4C_3 was chromatographed on an ODS column with MeOH/H_2O (40:60), then purified by HPLC with MeOH/H_2O (46:54), to yield **5** (16 mg, t_R = 48.6 min) and **6** (21 mg, t_R = 52.8 min). Fraction A_4C_4 was purified by HPLC with MeOH/H_2O (45:55) to yield **3** (25 mg, t_R = 47.8 min).

Illioliganone A (1): colorless oil; $[\alpha]^{25}_D$ −11.4 (*c* 0.13, CH_3OH); UV (MeOH) λ_{max} 230 (sh), 260 nm; CD (MeOH) λ_{max} ($\Delta\varepsilon$) 231 (1.62), 261 (−2.51), 296 (0.05), 336 (−0.90) nm; IR (KBr) ν_{max} 3448, 2971, 1744, 1672, 1339, 1130, 1042, 921 cm^{-1}; ^1H and ^{13}C NMR data, see Table 1; ESIMS (positive) *m/z* 273.1 $[M + Na]^+$; HRFABMS (positive) *m/z* 273.1100 $[M + Na]^+$ (calcd for $C_{14}H_{18}O_4Na$, 273.1097).

Illioliganone B (2): colorless oil; $[\alpha]^{20}_D$ −12.5 (*c* 0.28, MeOH); UV (MeOH) λ_{max} 245, 295 nm; CD (MeOH) λ_{max} ($\Delta\varepsilon$) 280 (4.66), 329 (−3.47) nm; IR (KBr) ν_{max} 3422, 2976, 1675, 1615, 1409, 1180, 912 cm^{-1}; ^1H and ^{13}C NMR data, see Table 1; ESIMS (positive) *m/z* 303.1 $[M + Na]^+$,; HRESIMS (positive) *m/z* 281.1388 $[M + H]^+$ (calcd for $C_{15}H_{21}O_5$, 281.1383).

Illioliganone C (3): colorless oil; $[\alpha]^{20}_D$ −23.1 (*c* 0.31, MeOH); UV (MeOH) λ_{max} 248, 308 nm; CD (MeOH) λ_{max} ($\Delta\varepsilon$) 247 (0.90), 282 (0.74), 325 (−4.14) nm; IR (KBr) ν_{max} 3391, 2970, 1710, 1650, 1642, 1612, 1413, 1227, 826 cm^{-1}; ^1H and ^{13}C NMR data, see Table 1; ESIMS (positive) *m/z* 303.1 $[M + Na]^+$; HRESIMS (positive) found 281.1385 $[M + H]^+$ (calcd for $C_{15}H_{21}O_5$, 281.1383).

Oligandriortholactone (7): white, amorphous powder; $[\alpha]^{25}_D$ +10.3 (*c* 0.11, MeOH); IR (KBr) ν_{max} 3408, 2944, 1709, 1602, 1585, 1452, 1270, 913, 712 cm^{-1}; ^1H and ^{13}C NMR data, see Table 2; ESIMS (positive) *m/z* 473.1 $[M + Na]^+$; HRESIMS (positive) *m/z* 473.1772 $[M + Na]^+$ (calcd for $C_{23}H_{30}O_9Na$, 473.1782).

Determination of Absolute Configuration of the 11,12-Diol Moieties in Compounds 2 and 3 by Snatzke's Method. Dimolybdenum tetracetate was purchased from Acros. DMSO of spectroscopy grade was purchased from Beijing Chemical Company, China, and dried with 4 Å molecular sieves. According to the published approach,[11] ca. 1:1 diol/$Mo_2(OAc)_4$ mixtures were subjected to CD measurements of **2** and **3**, at concentrations of 0.24 and 0.61 mg/mL, respectively. The first CD spectrum was recorded immediately after mixing, and its time evolution was monitored until stationary (about 30 min after mixing). The inherent CD was subtracted. The observed sign of the diagnostic band at 310 nm in the induced CD spectrum was correlated to the absolute configuration of the 11,12-diol moiety.

Anti-inflammatory Activity Assay.[16] The anti-inflammatory activities of compounds **1**−**8** were assayed by measuring the inhibition of the platelet-activating factor (PAF)-induced release of β-glucuronidase from rat polymorphonuclear leukocytes (PMNs) in vitro. Briefly, test compounds were dissolved in DMSO at a concentration of 0.1 M and diluted with RPMI-1640 to 10^{-3} mol/L when used. The suspension of rat PMNs (245 μL) at a density of 2.5×10^6 cells mL^{-1} and test samples (2.5 μL) was incubated at 37 °C for 15 min and for another 5 min after the addition of 1 mM cytochalasin B (2.5 μL). Subsequently 2.5 μL of 0.2 μM PAF was added. The reaction was terminated in an ice-bath after10 min. The supernatant was obtained by centrifugation at 4000 rpm for 5 min. Then 25 μL of supernatant and 2.5 mM phenolphthalein glucuronic acid (25 μL) were incubated with 100 μL of 0.1 M HOAc buffer (pH 4.6) at 37 °C, 5% CO_2 for 18 h. The reaction was completed on addition of 0.3 M NaOH (150 μL). The absorbance was read at 550 nm, and the inhibitory ratio (IR) was calculated as follows: IR (%) = $(A_{PAF} - A_t)/(A_{PAF} - A_C) \times 100\%$, where A_{PAF}, A_t, and A_c refer to the cell level of PAF, test compounds, and control groups, respectively. Ginkgolide B was used as the positive control.

Acknowledgment. This project was supported by the National Fund of Science for Distinguished Young Scholars (No. 30625040) and the '973' Project (No. 2004CB518906). The authors are grateful to the Department of Instrumental Analysis, Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, for measuring the IR, UV, NMR, and MS spectra.

Supporting Information Available: 1D and 2D NMR spectra of compounds **1**, **2**, **3**, and **7** and CD spectra of compounds **1**, **2**, and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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NP9001702