Phochinenins A – F, Dimeric 9,10-Dihydrophenanthrene Derivatives, from *Pholidota chinensis*

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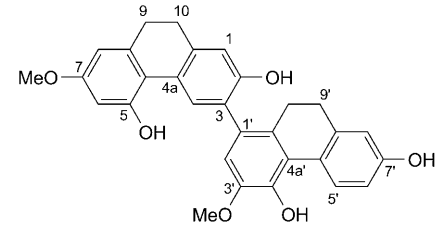
Six new compounds, phochinenins A – F (**1** – **6**), dimerized from 9,10-dihydrophenanthrene and dihydrostilbene through direct coupling or an oxygen bridge, along with eight known compounds, were isolated from the whole plants of *Pholidota chinensis*. Their structures were elucidated on the basis of extensive spectroscopic investigations (1D-, 2D-NMR, and HR-EI-MS).

Introduction. – *Pholidota chinensis* LINDL. (Orchidaceae), called 'shi xian tao' in Chinese, is a perennial herb distributed in Fujian, Guangdong, Guangxi, and Yunnan provinces [1]. The whole plant has been used as a folk medicine for the treatment of hypertension, dizziness, headache, and cough [1]. A marketed syrup made from the EtOH extract exhibited obvious activity to treat headache without side effects [2]. Recently, the EtOH extract of the whole plant was reported to have an inhibitory activity on the central nervous system [3]. Phytochemical investigations have revealed triterpenoids, cyclopholidonol, and cyclopholidone from this plant [4]. A recent study of *P. yunnanensis* ROLFE has led to the isolation of bis-benzyldihydrophenanthrene ether derivatives exhibiting inhibitory effects on nitric oxide production [5].

The present paper describes the isolation and characterization of six new compounds, phochinenins A – F (**1** – **6**, resp.), which were dimerized from 9,10-dihydrophenanthrene and dihydrostilbene through direct C – C coupling or an oxygen bridge, along with eight known compounds, flavanthrin (**7**) [6], blestrin A (**8**) [7], phoyunnanin D (**9**) [5], coelonin (**10**) [8a][8b], lusianthridin (**11**) [9], 3,4′-dihydroxy-3′,5-dimethoxybibenzyl (**12**) [10], thunalbene (**13**) [11], and batatasin III (**14**) [12] from the whole plant of *P. chinensis*. The structural elucidation of **1** – **6** was accomplished on the basis of spectroscopic data, especially 2D-NMR.

Results and Discussion. – Phochinenin A (**1**) was obtained as a brown amorphous powder. The molecular formula $C_{30}H_{26}O_6$ was determined by HR-EI-MS (*m*/*z* 482.1734 (M^+); calc. 482.1729). The maximal UV absorptions at 216, 279, and 297 nm indicated a 9,10-dihydrophenanthrene derivative [13]. The IR spectrum showed the presence of a OH group (3423 cm^{-1}) and aromatic rings (1610, 1465 cm^{-1}). The ^{13}C-NMR (*Table 1*) and DEPT spectra, combined with the HSQC spectrum, showed signals for two MeO groups, four CH_2 groups, and 24 aromatic C-atoms, including eight secondary aromatic C-atoms, six oxygenated aromatic C-atoms, and ten quarternary aromatic C-atoms. The



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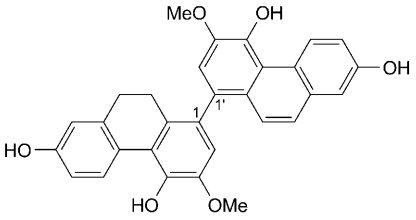

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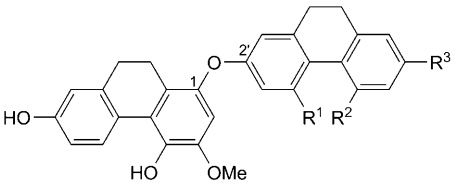
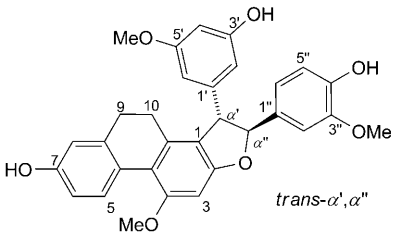


3 R^1 = H, R^2 = MeO, R^3 = OH
4 R^1 = H, R^2 = OH, R^3 = MeO
5 R^1 = MeO, R^2 = H, R^3 = OH



rac-**6**

Table 1. *^{13}C-NMR Data of* **1**–**5** (δ in ppm)

	1[a][c]	**2**[a][d]	**3**[b][d]	**4**[a][c]	**5**[a][c]		**1**[a][c]	**2**[a][d]	**3**[b][d]	**4**[a][c]	**5**[a][c]
C(1)	115.9	115.2	133.6	135.0	134.2	C(1′)	118.7	112.6	114.7	114.7	107.6
C(2)	154.2	99.7	100.6	101.2	101.4	C(2′)	99.7	100.1	157.6	156.9	159.3
C(3)	122.6	159.1	156.0	153.6	152.5	C(3′)	158.6	160.5	113.3	113.3	99.1
C(4)	133.4	156.3	150.0	152.8	153.5	C(4′)	155.3	154.3	130.2	130.4	159.5
C(4a)	140.2	142.7	134.2	134.6	134.7	C(4a′)	141.8	135.2	140.4	140.7	142.0
C(4b)	142.3	141.1	140.2	140.7	140.5	C(4b′)	141.3	134.9	141.9	142.5	141.0
C(5)	156.8	130.8	130.5	130.9	130.7	C(5′)	130.8	130.6	159.3	158.6	130.5
C(6)	101.9	113.8	114.0	114.2	113.9	C(6′)	113.8	117.6	99.5	101.9	114.1
C(7)	160.2	156.4	156.8	157.0	156.7	C(7′)	156.5	155.7	158.1	160.5	156.7
C(8)	106.5	115.0	115.3	115.5	115.3	C(8′)	115.1	112.4	108.6	106.5	115.3
C(8a)	116.6	126.8	125.8	128.6	126.3	C(8a′)	127.0	126.0	116.2	116.4	126.1
C(9)	32.4	31.3	30.7	31.0	31.4	C(9′)	31.5	128.7	31.6	32.3	30.8
C(10)	31.4	28.6	24.4	24.6	24.3	C(10′)	29.2	125.9	31.1	31.7	32.1
C(10a)	127.0	118.1	117.5	116.7	116.6	C(10a′)	118.0	117.1	128.1	126.6	118.7
*Me*O–C(3)		56.4	56.4	55.8	55.9	*Me*O–C(3′)	56.4	56.3			
*Me*O–C(4)						*Me*O–C(4′)					56.6
*Me*O–C(5)						*Me*O–C(5′)			56.1		
*Me*O–C(7)	55.9					*Me*O–C(7′)				56.6	

[a]) In CD_3OD. [b]) In (D_6)acetone. [c]) At 100 MHz. [d]) At 125 MHz.

^{1}H-NMR spectrum (*Table 2*) showed signals of two aromatic *meta*-coupled H-atoms at δ(H) 6.31 (*d*, $J = 2.4$, 1 H) and 6.35 (*d*, $J = 2.4$, 1 H), an *ABX* system at δ(H) 6.59 (*d*, $J = 2.4$, 1 H), 6.63 (*dd*, $J = 8.6$, 2.4, 1 H), and 8.03 (*d*, $J = 8.6$, 1 H), three *singlet* aromatic H-atoms at δ(H) 6.57 (*s*, 1 H), 6.77 (*s*, 1 H), and 8.03 (*s*, 1 H), two MeO

Table 2. *^{1}H-NMR Data of* **1**–**5** (δ in ppm, J in Hz)

	1[a])[c])	**2**[a])[d])	**3**[b])[d])	**4**[a])[c])	**5**[a])[d])
H–C(1)	6.77 (*s*)				
H–C(2)		6.67 (*s*)	6.67 (*s*)	6.54 (*s*)	6.57 (*s*)
H–C(4)	8.03 (*s*)				
H–C(5)		8.10 (*d*, *J* = 8.9)	8.12 (*d*, *J* = 8.5)	8.22 (*d*, *J* = 8.6)	8.24 (*d*, *J* = 8.3)
H–C(6)	6.35 (*d*, *J* = 2.4)	6.66 (*dd*, *J* = 8.9, 3.0)	6.71 (*dd*, *J* = 8.5, 2.7)	6.67 (*dd*, *J* = 8.6, 2.8)	6.68 (*dd*, *J* = 2.3, 8.3)
H–C(8)	6.31 (*d*, *J* = 2.4)	6.58 (*d*, *J* = 3.0)	6.69 (*d*, *J* = 2.7)	6.62 (*d*, *J* = 2.8)	6.64 (*d*, *J* = 2.3)
CH_2(9)	2.73 (*s*)	2.44–2.48 (*m*)	2.56–2.60 (*m*)	2.63 (*s*)	2.63 (*s*)
CH_2(10)	2.73 (*s*)	2.20–2.24 (*m*)	2.56–2.60 (*m*)	2.63 (*s*)	2.63 (*s*)
H–C(1′)			6.67 (*d*, *J* = 2.8)	6.58 (*d*, *J* = 2.8)	6.24 (*d*, *J* = 2.6)
H–C(2′)	6.57 (*s*)	6.94 (*s*)			
H–C(3′)			6.64 (*dd*, *J* = 8.8, 2.8)	6.61 (*dd*, *J* = 8.5, 2.8)	6.46 (*d*, *J* = 2.6)
H–C(4′)			8.11 (*d*, *J* = 8.8)	8.19 (*d*, *J* = 8.5)	
H–C(5′)	8.03 (*d*, *J* = 8.6)	9.45 (*d*, *J* = 9.4)			8.03 (*d*, 9.5)
H–C(6′)	6.63 (*dd*, *J* = 8.6, 2.4)	7.12 (*dd*, *J* = 2.7, 9.4)	6.46 (*d*, *J* = 2.3)	6.33 (*s*)	6.64 (*dd*, *J* = 9.5, 2.6)
H–C(8′)	6.59 (*d*, *J* = 2.4)	7.11 (*d*, *J* = 2.7)	6.38 (*d*, *J* = 2.3)	6.33 (*s*)	6.63 (*d*, *J* = 2.6)
CH_2(9′) or H–C(9′)	2.48–2.52 (*m*)	7.40 (*d*, *J* = 9.0)	2.46 (*s*)	2.64–2.68 (*m*)	2.62–2.66 (*m*)
CH_2(10′) or H–C(10′)	2.44–2.48 (*m*)	7.18 (*d*, *J* = 9.0)	2.46 (*s*)	2.64–2.68 (*m*)	2.62–2.66 (*m*)
MeO–C(3)		3.95 (*s*)	3.89 (*s*)	3.74 (*s*)	3.77 (*s*)
MeO–C(7)	3.75 (*s*)				
MeO–C(3′)	3.88 (*s*)	4.15 (*s*)			
MeO–C(4′)					3.79 (*s*)
MeO–C(5′)			3.83 (*s*)		
MeO–C(7′)				3.75 (*s*)	

[a]) In CD_3OD. [b]) In (D_6)acetone. [c]) At 300 MHz. [d]) At 600 MHz.

groups at δ(H) 3.75 (*s*, 3 H) and 3.88 (*s*, 3 H), two *singlet* CH_2 groups at δ(H) 2.73 (*s*, 4 H), and two *multiplet* CH_2 groups at δ(H) 2.48–2.52 (*m*, 2 H) and 2.44–2.48 (*m*, 2 H). All the above data suggested an asymmetrical structure for a dimeric 9,10-dihydrophenanthrene derivative. The fragment ion at *m*/*z* 241 in the EI-MS indicated the same elemental composition $C_{15}H_{13}O_3$ for the two monomers. A comprehensive analysis of the HSQC, HMBC, and ROESY spectra permitted the complete assignment of H- and C-atom signals for each monomer (*Fig. 1*). HMBC Correlations of CH_2(10)/C(1) and C(9), CH_2(9)/C(8), H–C(8)/C(9), and H–C(1)/C(10) indicated a 2,3,5,7-substituted 9,10-dihydrophenanthrene fragment. The other monomer was found to be substituted at C(1′), C(3′), C(4′), and C(7′) by the HMBC correlations of CH_2(10′)/C(1′) and C(9′), CH_2(9′)/C(8′), H–C(8′)/C(9′), and H–C(2′)/C(10a′). The two monomers were coupled directly by C(3) and C(1′) on the basis of the long range HMBC correlations of H–C(4)/C(1′), H–C(10′)/C(1′), and H–C(2′)/C(3), which was further confirmed by the up-field shift of CH_2(9′) (δ(H) 2.48–2.52) and CH_2(10′) (δ(H) 2.44–2.48) by comparison with those of CH_2(9) (δ(H) 2.73) and CH_2(10) (δ(H)

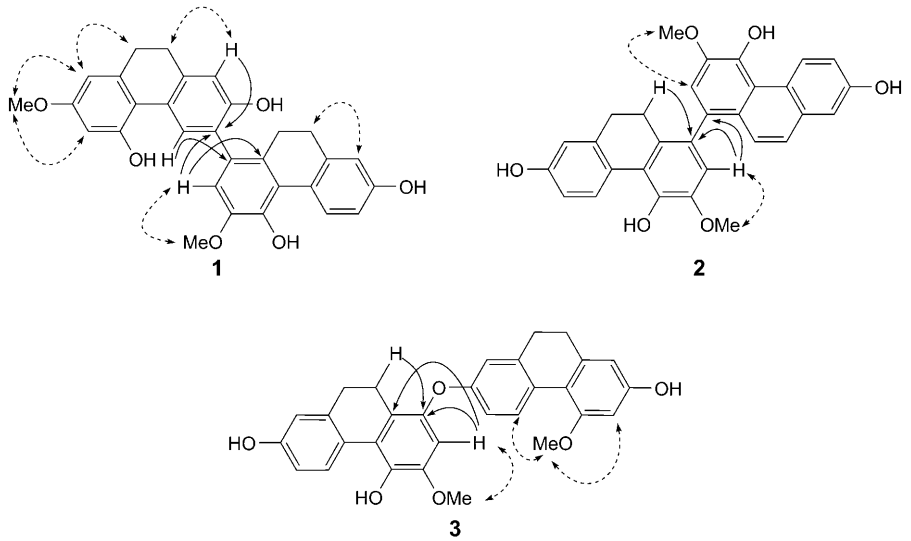


Fig. 1. *Key HMBC* (H→C) *and ROESY* (←----→) *correlations for* **1**–**3**

2.73). In the ROESY spectrum, the correlations of MeO (δ(H) 3.75)/H–C(6) and H–C(8), and MeO (δ(H) 3.88)/H–C(2′) indicated that the two MeO groups were located at C(7) and C(3′), respectively. Therefore, **1** was established as 9,9′,10,10′-tetrahydro-3,7′-dimethoxy-1,3′-biphenanthrene-2′,4,5′,7-tetrol.

Phochinenin B (**2**), a brown amorphous powder, showed UV absorptions at 211, 263, 357, and 375 nm. The molecular formula was determined to be $C_{30}H_{24}O_6$ by HR-EI-MS (*m*/*z* 480.1575 (M^+); calc. 480.1573), 2 mass units less than that of **1**. The ^{13}C-NMR (*Table 1*) and DEPT spectra showed signals of two aromatic C-atoms instead of two CH_2 groups by comparison with those of **1**. In the ^{1}H-NMR spectrum (*Table 2*), the presence of a pair of *cis*-configured H-atoms at δ(H) 7.40 (*d*, J = 9.0, 1 H) and 7.18 (*d*, J = 9.0, 1 H) and the absence of two CH_2 groups were observed. All these data, combined with analysis of HSQC, HMBC, and ROESY spectra (*Fig. 1*), suggested a dimeric structure composed of a 1,3,4,7-tetrasubstituted 9,10-dihydrophenanthrene fragment and a 1′,3′,4′,7′-tetrasubstituted phenanthrene fragment. HMBC Correlations of CH_2(10)/C(1), H–C(2)/C(1′), and H–C(10′)/C(1′) indicated that the two fragments were linked by C(1) and C(1′). The ROESY correlations of MeO (δ(H) 3.95)/H–C(2) and MeO (δ(H) 4.15)/H–C(2′) indicated that two MeO groups were located at C(3) and C(3′), respectively. Thus, the structure of **2** was fully established as 9,10-dihydro-3,3′-dimethoxy-1,1′-biphenanthrene-4,4′,7,7′-tetrol.

Phochinenin C (**3**) was obtained as a brown-yellow amorphous powder and its molecular formula was assigned as $C_{30}H_{26}O_6$ on the basis of HR-EI-MS data (*m*/*z* 482.1734 (M^+); calc. 482.1729). The UV spectrum showed characteristic absorptions for a 9,10-dihydrophenanthrene derivative at 211, 279, and 295 nm. The ^{13}C-NMR (*Table 1*), DEPT, and HSQC spectra disclosed the presence of 30 C-atoms, which were ascribed to two MeO groups, four CH_2 groups, and 24 aromatic C-atoms consisting of nine secondary aromatic C-atoms, eight quaternary aromatic C-atoms, and seven

oxygenated aromatic C-atoms. Six O-atoms (as indicated in its molecular formula) in contrast to seven oxygenated C-atoms suggested the presence of an ether group. The NMR similarities between **3** and phoyunnanin E [5], a bis(9,10-dihydrophenanthrene) ether, indicated that they shared the same structural skeleton. The differences were the positions of two MeO substituents, which were deduced to be at C(3) and C(5′) in **3** by the ROESY experiment (*Fig. 1*), respectively.

Phochinenins D and E (**4** and **5**) were determined to possess the same molecular formula $C_{30}H_{26}O_6$ as **3**. Their NMR spectra (*Tables 1* and *2*) strongly resembled those of **3**, suggesting the same bis(9,10-dihydrophenanthrene) ether skeleton in their molecules. The substitution patterns of 9,10-dihydrophenanthrene were determined by their respective ROESY and HMBC spectra. The location of the MeO substituents were determined to be C(3) and C(7′) in **4**, and C(3) and C(4′) in **5** by the ROESY correlations (MeO (δ(H) 3.74)/H–C(2), and MeO (δ(H) 3.75)/H–C(6′) and H–C(8′) in **4**; MeO (δ(H) 3.77)/H–C(2), and MeO (δ(H) 3.79)/H–C(3′) and H–C(5′) in **5**).

Phochinenin F (**6**) was determined to possess the molecular formula $C_{31}H_{28}O_7$ by HR-EI-MS (*m/z* 512.1842 (M^+); calc. 512.1835), with 18 degrees of unsaturation. The maximal UV absorptions were observed at 205 and 282 nm. The IR spectrum showed the presence of OH groups at 3415 cm^{-1}, and aromatic rings at 1610 and 1456 cm^{-1}. The ^{13}C-NMR (*Table 3*), DEPT and HSQC spectra revealed 31 C-atom signals ascribed to three MeO groups, two CH_2 groups, one CH group, and one oxygenated CH group, as well as 24 aromatic C-atoms consisting of ten secondary aromatic C-atoms, seven oxygenated aromatic C-atoms, and seven quaternary aromatic C-atoms. The ^{1}H-NMR spectrum (*Table 3*) showed signals of two pairs of *ABX* systems ((δ(H) 8.04 (*d*, *J* = 8.6, 1 H), 6.64 (*dd*, *J* = 8.6, 2.4, 1 H), and 6.60 (*d*, *J* = 2.4, 1 H)); (6.91 (*d*, *J* = 1.6, 1 H), 6.79 (*dd*, *J* = 7.9, 1.6, 1 H), and 6.81 (*d*, *J* = 7.9, 1 H))), three *meta*-coupled aromatic H-atoms (δ(H) 6.20 (*d*, *J* = 1.5, 1 H), 6.28 (*dd*, *J* = 2.1, 1.5, 1 H), and 6.22 (*d*, *J* = 2.1, 1 H)), a *singlet* H-atom (δ(H) 6.63 (*s*, 1 H)), three MeO groups (δ(H) 3.71 (*s*), 3.84 (*s*),

Table 3. *^{1}H-* (600 MHz) *and ^{13}C-* (100 MHz) *NMR Data of Phochinenin F* (**6**) (in CD_3OD). δ in ppm, *J* in Hz.

	δ(H)	δ(C)		δ(H)	δ(C)
C(1)		120.2	C(1′)		147.5
C(2)		161.1	H–C(2′)	6.22 (*d*, *J* = 2.1)	106.3
H–C(3)	6.63 (*s*)	94.4	C(3′)		163.3
C(4)		160.0	H–C(4′)	6.28 (*dd*, *J* = 1.5, 2.1)	101.3
C(4a)		138.3	C(5′)		160.6
C(4b)		140.8	H–C(6′)	6.20 (*d*, *J* = 1.5)	108.7
H–C(5)	8.04 (*d*, *J* = 8.6)	130.7	H–C(α')	4.43 (*d*, *J* = 6.5)	59.0
H–C(6)	6.64 (*dd*, *J* = 2.4, 8.6)	114.1	H–C(α")	5.37 (*d*, *J* = 6.5)	95.6
C(7)		156.7	C(1″)		135.0
H–C(8)	6.60 (*d*, *J* = 2.4)	115.4	H–C(2″)	6.91 (*d*, *J* = 1.6)	110.8
C(8a)		118.9	C(3″)		149.6
CH_2(9)	2.48–2.50 (*m*)	31.2	C(4″)		148.1
CH_2(10)	2.36–2.40 (*m*), 2.20–2.24 (*m*)	29.8	H–C(5″)	6.81 (*d*, *J* = 7.9)	116.7
C(10a)		126.6	H–C(6″)	6.79 (*dd*, *J* = 1.6, 7.9)	120.3
MeO–C(4)	3.92 (*s*)	56.8	MeO–C(3′)	3.84 (*s*)	56.9
			MeO–C(3″)	3.71 (*s*)	56.1

and 3.92 (*s*)), a pair of CH groups (δ(H) 5.37 (*d*, $J = 6.5$, 1 H) and 4.43 (*d*, $J = 6.5$, 1 H)), and two CH_2 groups (δ(H) 2.48–2.50 (*m*, 2 H), 2.36–2.40 (*m*, 1 H), and 2.20–2.24 (*m*, 1 H)). All data indicated the presence of a 9,10-dihydrophenanthrene fragment and a dihydrostilbene fragment possessing substituents at C(α') and C(α''). HMBC correlations from CH_2(10), H–C(α'), and H–C(α'') to C(1) (δ(C) 120.2) indicated that these two segments were combined at C(1) and C(α') (*Fig. 2*). The low-field chemical shifts of C(2) (δ(C) 161.1) and C(α'') (δ(C) 95.6), corresponding to one oxygenated aromatic C-atom and one oxygenated CH group, allowed only a linkage from C(2) to C(α'') *via* an O-atom due to the remaining degree of unsaturation, which was further confirmed by the HMBC correlation of H–C(α'')/C(2). Thus, a furan ring was constructed with C(1), C(2), C(α'), and C(α''). The three MeO groups were assigned by the ROESY experiment (*Fig. 2*,*a*).

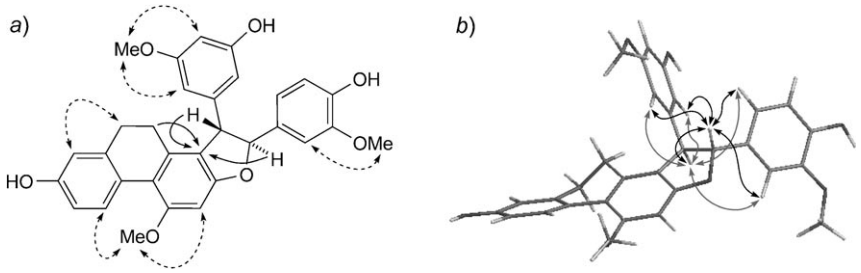


Fig. 2. a) *Key HMBC* (H→C) *and some ROESY* (←- - -→) *correlations of* rac-**6**. b) *Key ROESY correlations in the 3D structure of* rac-**6** *that was generated with an optimized energy minimization using MM2*

The optical rotation of **6** was zero, and no *Cotton* effects were detected in the CD spectrum, suggesting that the compound was racemic. In the ^{1}H- and ^{13}C-NMR spectra, the only one set of observed resonances excluded a mixture of *cis-trans* isomers and suggested **6** to be either the *trans*(α',α'')- or the *cis*(α',α'')-racemate. The ROESY correlations (*Fig. 2*,*b*) observed between the two H-atoms (H–C(α'), H–C(α'')), and some aromatic H-atoms supported a *trans*-configuration of H–C(α') and H–C(α'') [14a]. The interatomic nonbonded distance of the key atoms on the basis of a 3D model was listed in *Table 4*. In addition, the coupling constant $J(\alpha',\alpha'') = 6.5$ Hz was in agreement with literature values for the *trans* configuration [14]. Therefore, **6** was

Table 4. *The Interatomic Non-Bonded Distance of the Key Atoms of* **6** *Based on a 3D Model*

Atoms	Distance [Å]
α', α''	3.109
α', 2′	2.379
α', 6′	3.778
α', 2″	3.348
α', 6″	3.655
α', 2′	4.296
α', 6′	2.466
α'', 2″	3.626
α'', 6″	2.533

determined to be (2*RS*,3*RS*)-3-(3-hydroxy-5-methoxyphenyl)-2-(4-hydroxy-3-methoxyphenyl)-10-methoxy-2,3,4,5-tetrahydrophenanthro[2,1-*b*]furan-7-ol.

In conclusion, nine dimeric 9,10-dihydrophenanthrene derivatives, **1**–**9**, are reported from *P. chinensis* for the first time. To the best of our knowledge, phochinenin F (**6**) was the first example in the plant kingdom that a furan ring bridged a 9,10-dihydrophenanthrene and a dihydrostilbene. The optical rotation data of compounds **1** and **2** were zero, which indicated the lack of significant steric hindrance at the *ortho* positions around the biaryl axis in this class of compounds. A biosynthetic conversion of stilbenes (dihyrostilbenes) into phenanthrenes (dihydrophenanthrenes) was postulated in previous studies [15]. From this work, we can see that such monomers can be further polymerized into a series of 9,10-dihydrophenanthrene and dihydrostilbene dimers probably through carbon free radical and oxygen free radical reactions.

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Experimental Part

General. Column chromatography (CC): commercial silica gel (SiO_2; 200–300 and 300–400 mesh, *Qing Dao Hai Yang Chemical Group Co.*). TLC: Precoated SiO_2 GF_{254} plates (*Yan Tai Chemical Industry*). Prep. HPLC: *PrepStar SD-1* solvent delivery modules, a *ProStar UV-VIS 320* detector and a *ProStar 701* Fraction Collector (all from *Varian*, Walnut Creek, CA, USA); *LinChrospher 100 RP-18* (*Merck*, Darmstadt, Germany) column (25 × 220 mm; 12 μm). Optical rotation: *Perkin-Elmer 341* polarimeter. UV Spectra: *Hewlett-Packard 8452A* diode-array spectrophotometer; λ_{max} in nm (log ε). IR Spectra: *Nicolet Magna-FT-IR-750* spectrometer; ν_{max} in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker AM-400* and *INVOA-600* NMR spectrometers; chemical shifts, δ in ppm, with residual MeOH (δ(H) 3.30, δ(C) 49.0) or acetone (δ(H) 2.05, δ(C) 29.92) as internal standard, coupling constant *J* in Hz, assignments supported by ^1H,^1H-COSY, HSQC, HMBC, and ROESY experiments. EI: *Finnigan MAT-95* mass spectrophotometer; in *m*/*z*. ESI- and HR-ESI-MS: *Micromass LC-MS-MS* apparatus; in *m*/*z*.

Plant Material. The whole plants of *P. chinensis* were collected in Xichou country, Yunnan Province, P. R. China, in April 2004 and identified by *Jingui Shen*, Shanghai Institute of Materia Medica, Chinese Academy of Sciences. A voucher specimen (No. 20050325) is deposited in the Herbarium of the Shanghai Institute of Materia Medica.

Extraction and Isolation. Powdered and air-dried whole plants of *P. chinensis* (1.84 kg) were percolated with 95% EtOH (3 × 5 l) at r.t. for 9 d. After evaporation of EtOH *in vacuo*, the residue was dissolved in H_2O (6.0 l) and then extracted with petroleum ether (PE) (60–90°), AcOEt and BuOH (each 3 × 1 l). The PE fraction (93 g) was subjected to CC over SiO_2, eluted with a gradient of PE/AcOEt 100:1 to 0:1 to yield nine fractions (*Fr. 1*–*Fr. 9*). *Fr. 6* (7.5 g) was subjected to SiO_2 CC and eluted with a gradient of $CHCl_3$/MeOH (200:1 to 200:5) and purified by *Sephadex LH-20* ($CHCl_3$/MeOH 6:4) to give **10** (140 mg), **11** (35 mg), **12** (45 mg), and **13** (43 mg). *Fr. 8* (2.0 g) was subjected to SiO_2 CC with $CHCl_3$/MeOH (100:4) to yield subfractions *Fr. 8A*–*Fr. 8D*. *Fr. 8A* (400 mg) was separated by SiO_2 CC with $CHCl_3$/MeOH (100:4) and then *Sephadex LH-20* ($CHCl_3$/MeOH 1:1) to give **8** (16 mg). The residue of *Fr. 8A* was separated by Pre-HPLC (MeCN/H_2O 28%–60%, 15 ml/min, 290 nm) to give **6** (34 mg). *Fr. 8B* (400 mg) was separated by CC ($CHCl_3$/MeOH 100:1) and *Sephadex LH-20* ($CHCl_3$/MeOH 6:4) to give **1** (39 mg) and **14** (14 mg). *Fr. 9* (4.0 g) was subjected to SiO_2 CC with a gradient of $CHCl_3$/MeOH (100:1 to 100:3) to afford subfractions *Fr. 9A*–*Fr. 9E*. *Fr. 9A* (800 mg) was separated by Pre-HPLC (MeCN/H_2O 28%–56%, 15 ml/min, 320 nm) and then purified by a *Sephadex LH-20* column (MeOH) to give **1** (11 mg) and **5** (48 mg). *Fr. 9B* (400 mg) was separated by Pre-HPLC (MeCN/H_2O 25%–65%, 15 ml/min, 320 nm) to give **1** (80 mg) and **7** (85 mg). The residue of *Fr. 9B* was further separated by *Sephadex LH-20* (MeOH) to yield **2** (4 mg) and **7** (30 mg). *Fr. 9D* (430 mg) was separated by Pre-HPLC (MeCN/H_2O 20%–55%, 15 ml/min, 290 nm) and purified by *Sephadex LH-20* (MeOH) to yield **3** (57 mg), **4** (11 mg), **8** (63 mg), and **9** (24 mg).

Phochinenin A (=*9,9′,10,10′-Tetrahydro-3,7′-dimethoxy-1,3′-biphenanthrene-2′,4,5′,7-tetrol*; **1**). Brown amorphous powder. $[\alpha]_D^{25} = 0$ ($c = 0.3$, MeOH). UV (MeOH): 216 (4.71), 279 (4.52), 297 (4.41). IR (KBr): 3423, 1610, 1465, 1195, 1161. ^{1}H- and ^{13}C- NMR: *Tables 1* and *2*. EI-MS: 482 (M^+), 241 (16), 227 (9), 197 (5), 181 (4), 165 (2), 115 (2), 76 (2), 55 (2). HR-EI-MS: 482.1734 (M^+, $C_{30}H_{26}O_6^+$; calc. 482.1729).

Phochinenin B (=*9,10-Dihydro-3,3′-dimethoxy-1,1′-biphenanthrene-4,4′,7,7′-tetrol*; **2**). Brown amorphous powder. $[\alpha]_D^{25} = 0$ ($c = 0.2$, MeOH). UV (MeOH): 211 (4.60), 263 (4.66), 357 (3.48), 375 (3.53). IR (KBr): 3423, 1610, 1585, 1459, 1209, 1161. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. EI-MS: 480 (M^+), 240 (40), 241 (16), 225 (16), 197 (16), 181 (8), 150 (5), 115 (5), 87 (2), 58 (8). HR-EI-MS: 480.1575 (M^+, $C_{30}H_{24}O_6^+$; calc. 480.1573).

Phochinenin C (=*9,10-Dihydro-8-[(9,10-dihydro-7-hydroxy-5-methoxyphenanthren-2-yl)oxy]-6-methoxyphenanthrene-2,5-diol*; **3**). Brown-yellow amorphous powder. UV (MeOH): 211 (4.70), 279 (4.51), 295 (4.40). IR (KBr): 3430, 1627, 1382, 1060. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. EI-MS: 482 (M^+), 242 (46), 226 (56), 199 (17), 181 (17), 152 (12), 115 (9), 91 (3), 55 (5). HR-EI-MS: 482.1734 (M^+, $C_{30}H_{26}O_6^+$; calc. 482.1729).

Phochinenin D (=*9,10-Dihydro-8-[(9,10-dihydro-5-hydroxy-7-methoxyphenanthren-2-yl)oxy]-6-methoxyphenanthrene-2,5-diol*; **4**). Brown amorphous powder. $[\alpha]_D^{25} = +0.008$ ($c = 0.3$, MeOH). UV (MeOH): 200 (5.61), 278 (5.58), 297 (5.44). IR (KBr): 3423, 1614, 1484, 1224. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. EI-MS: 482 (M^+), 242 (100), 227 (56), 181 (22), 152 (9), 115 (8), 91 (7), 76 (9), 63 (8), 55 (9). HR-EI-MS: 482.1726 (M^+, $C_{30}H_{26}O_6^+$; calc. 482.1729).

Phochinenin E (=*9,10-Dihydro-8-[(9,10-dihydro-7-hydroxy-4-methoxyphenanthren-2-yl)oxy]-6-methoxyphenanthrene-2,5-diol*; **5**). Brown amorphous powder. UV (MeOH): 279 (4.48). IR (KBr): 3405, 1612, 1459, 1222, 1151. ^{1}H- and ^{13}C-NMR: *Tables 1* and *2*. EI-MS: 482 (M^+), 242 (100), 227 (36), 199 (30), 181 (22), 152 (15), 115 (15), 99 (4), 76 (8), 55 (11). HR-EI-MS: 482.1721 (M^+, $C_{30}H_{26}O_6^+$; calc. 482.1729).

Phochinenin F (=*(2*RS*,3*RS*)-2,3,4,5-Tetrahydro-3-(3-hydroxy-5-methoxyphenyl)-2-(4-hydroxy-3-methoxyphenyl)-10-methoxyphenanthro[2,1-*b*]furan-7-ol*; **6**). Brown amorphous powder. $[\alpha]_D^{25} = 0$ ($c =$ 0.3, MeOH). UV (MeOH): 205 (4.88), 282 (4.35). IR (KBr): 3415, 1610, 1456, 1199, 1155. ^{1}H- and ^{13}C-NMR: *Table 3*. EI-MS: 512 (M^+), 482 (27), 466 (9), 375 (11), 357 (12), 241 (6), 149 (28), 101 (15), 69 (17), 59 (28). HR-EI-MS: 512.1842 (M^+, $C_{31}H_{28}O_7^+$; calc. 512.1835).

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