Chilianthins A—F, Six Triterpene Esters Having Dimeric Structures from *Rhoiptelea chiliantha* DIELS *et* HAND.-MAZZ.

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Received February 29, 1996; accepted April 25, 1996

Five triterpene-lignan esters, chilianthins A—E (2—6) and a triterpene-naphthalene carboxylic acid ester, chilianthin F (7), were isolated from the bark of *Rhoiptelea chiliantha* DIELS *et* HAND.-MAZZ. (Rhoipteleaceae), together with a known triterpene caffeate, 27-caffeoyloxy-3β-hydroxyolean-12-en-28-oic acid (myriceric acid B, 1). Their structures were elucidated on the basis of spectroscopic and chemical evidence. Chilianthins A (2), B (3), C (4) and E (6) were biomimetically synthesized from 1 by oxidative coupling.

Key words *Rhoiptelea chiliantha*; Rhoipteleaceae; chilianthin; triterpene-lignan ester; triterpene-naphthalene carboxylic acid ester; triterpene caffeate

Rhoiptelea chiliantha DIELS *et* HAND.-MAZZ. is the only species of the family Rhoipteleaceae, which is distributed in the southern China and northern Vietnam. Morphological, anatomical and palynological studies on this plant have led to several different opinions on the systematic position of the Rhoipteleaceae.[1] For chemotaxonomic reasons, we have investigated the chemical constituents of this plant and reported the structures of a rearranged ursane triterpene named rhoiptelic acid,[2] a lupane triterpene and two triterpene caffeates from the bark,[3] and dimeric ellagitannins formed by intermolecular oxidative C–C coupling from fruits and leaves.[4] Further studies on the chemical constituents of the bark of this plant led to the isolation of five triterpene-lignan esters named chilianthins A (**2**), B (**3**) (formerly named rhoipteleic acids A and B,[5] respectively), C (**4**), D (**5**) and E (**6**), and a triterpene-naphthalene carboxylic acid ester named chilianthin F (**7**), which possess dimeric structures, and a known triterpene caffeate, *i.e.* 27-caffeoyloxy-3β-hydroxyolean-12-en-28-oic acid (**1**). This paper presents a full account of the structure elucidation of these compounds.

Results and Discussion

The EtOH extract of the air-dried bark (4.5 kg) was partitioned between H_2O and ether. The ether layer was treated with MeOH, and the MeOH-soluble part was chromatographed over MCI-gel CHP 20P. The fractions positive to 2% $FeCl_3$–EtOH reagent were subjected to column chromatographies on silica gel, Chromatorex ODS and Bondapak C_{18} and further purified by preparative HPLC to afford a triterpene caffeate (**1**) and chilianthins A (**2**), B (**3**), C (**4**), D (**5**), E (**6**) and F (**7**).

Compound **1** was obtained as colorless needles from 80% MeOH and showed dark green coloration with 2% $FeCl_3$–EtOH reagent. The FAB-MS showed an $[M+H+glycerol]^+$ ion peak at *m/z* 727. The ^{13}C-NMR spectrum suggested the presence of a triterpene moiety and a caffeoyl group in the molecule, and the latter was confirmed by methanolysis (HCl–MeOH) of the trimethylate of **1** (**1a**), yielding methyl *trans*-3,4-dimethoxycinnamate (**1b**). The triterpene moiety was determined by alkaline hydrolysis (2.5% NaOH) of **1**, yielding a triterpene acid (**1c**), which was identified as 3β,27-dihydroxyolean-12-en-28-oic acid.[6] The location of the caffeoyl group in **1** was determined to be at the C-27 hydroxyl group on the basis of the downfield shifts of H-27 and C-27 compared with those of **1c**. Accordingly, **1** was concluded to be 27-caffeoyloxy-3β-hydroxyolean-12-en-28-oic acid. This compound has already been isolated from *Melianthus*[7] and *Myrica* plants and was recently named myriceric acid B; it was shown to have a weak endothelin antagonist activity.[8]

Chilianthins A (**2**) and B (**3**) were each isolated as a white powder positive to the $FeCl_3$ reagent. They were shown to have the same molecular formula of $C_{78}H_{106}O_{14}$ on the basis of positive FAB-MS (*m/z* 1267 $[M+H]^+$), elemental analyses and ^{13}C-NMR spectra showing signals arising from 78 carbons including 22 sp^2 carbons. The presence of two triterpene moieties with the same skeleton in each molecule was suggested by the ^{13}C-NMR signals, which appeared in pairs (see Table 1). The chemical shifts of these signals were closely related to those of **1c**, indicating that **2** and **3** have the same triterpene moieties as that of **1**. This was confirmed by alkaline hydrolyses of **2** and **3** with 10% NaOH, affording the triterpene **1c** as the sole non-polar product.

The remaining parts of the molecules of **2** and **3** were considered to be phenol carboxylic acid because of the dark green coloration of these compounds with the $FeCl_3$ reagent and the appearance of the carbon signals due to two aromatic rings, two conjugated carboxyls (δ 168.4, 169.3) and two non-conjugated carboxyls (δ 174.7, 174.4) in the ^{13}C-NMR spectra. In the ^{1}H-NMR spectra, the ABX-spin systems due to a catechol ring (H-5′, H-6′, H-2′), three one-proton singlets (H-4, H-5, H-8) and a pair of aliphatic proton signals (H-1, H-2) are similar to those of the lignan unit of rabdosiin isolated from plants of Labiatae and Boraginaceae.[9] These observations suggested the presence of a 1,2-dihydro-1-(3′,4′-dihydroxyphenyl)-6,7-dihydroxynaphthalene-2,3-dicarboxylic acid moiety in each molecule. On methylation with CH_2N_2, **2** and **3** gave hexamethylates (**2a** and **3a**, respectively), which were successively hydrolyzed with *p*-TsOH in benzene[10] to afford the lignan methyl ethers together with a tosylated triterpene derivative **2c**, the structure of which was assigned on the basis of ^{1}H- and ^{13}C-NMR and MS analyses. The

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Table 1. ^{13}C-NMR Spectral Data for Triterpene Moieties of **1**—**7** and **1c**

	1[a]	**1c**[a]	**2**[b]	**3**[b]	**4**[b]	**5**[c]	**6**[b]	**7**[d]
C-1	39.0 t	38.9 t	39.4 t	40.6 t	39.4	40.6	39.9 t	38.7
			40.1 t	41.2 t	40.1	40.6		
C-2	28.0 t	28.1 t	27.8 t	28.5 t	27.9	28.5	27.8 t	28.1
			27.8 t	28.7 t	27.9	29.0		
C-3	77.9 d	78.1 d	79.7 d	80.4 d	79.7	79.6	79.6 d	77.9
			79.7 d	80.4 d	79.7	80.1		
C-4	39.3 s	39.4 s	39.9 s	40.6 s	39.9	39.9	39.7 s	39.4
			39.9 s	40.8 s	39.9	40.3		
C-5	55.8 d	55.8 d	56.9 d	57.4 d	56.9	56.5	56.9 d	55.7
			57.1 d	57.9 d	57.2	57.5		
C-6	18.8 t	18.9 t	19.4 t	20.26 t	19.4	20.1	19.5 t	18.8
			19.4 t	20.34 t	19.5	20.2		
C-7	33.7 t	33.7 t	34.3 t	35.0 t	34.3	34.9	34.6 t	33.8
			34.9 t	35.7 t	34.9	35.3		
C-8	40.5 s	40.5 s	41.06 s	41.9 s	41.1	42.0	41.2 s	40.6
			41.14 s	41.9 s	41.2	42.1		
C-9	49.1 d	48.8 d	50.1 d	50.85 d	50.1	50.9	50.2 d	49.0
			50.4 d	50.90 d	50.4	50.9		
C-10	37.6 s	37.6 s	38.3 s	39.1 s	38.4	39.1	38.4 s	37.6
			38.3 s	39.3 s	38.4	39.2		
C-11	23.6 t	23.8 t	23.7 t	24.5 t	23.9	24.7	23.9 t	23.8
			23.8 t	24.7 t	23.9	24.7		
C-12	127.0 d	127.7 d	128.2 d	128.9 d	128.2	128.8	128.9 d	127.0
			128.7 d	129.1 d	128.8	129.2		
C-13	138.9 s	139.9 s	137.5 s	138.9 s	137.4	140.1	137.8 s	139.1
			137.9 s	139.6 s	137.9	141.6		
C-14	46.0 s	48.0 s	46.7 s	47.4 s	46.7	47.4	46.3 s	45.8
			46.9 s	47.7 s	47.0	47.6		
C-15	24.4 t	24.4 t	25.1 t	25.9 t	25.2	25.7	23.9 t	24.3
			25.5 t	26.1 t	25.5	26.0		
C-16	24.1 t	24.1 t	24.7 t	25.86 t	24.7	24.9	23.9 t	24.2
			24.7 t	25.94 t	24.7	25.1		
C-17	46.5 s	46.6 s	47.2 s	48.1 s	47.2	48.1	47.3 s	46.4
			47.4 s	48.3 s	47.5	48.2		
C-18	41.9 d	41.8 d	42.1 d	43.3 d	42.1	42.8	42.4 d	41.9
			42.4 d	43.5 d	42.5	43.3		
C-19	45.4 t	45.6 t	45.1 t	46.1 t	45.1	47.1	45.8 t	45.4
			45.4 t	46.3 t	45.5	47.1		
C-20	30.9 s	31.0 s	31.3 s	32.1 s	31.3	32.4	31.6 s	30.9
			31.6 s	32.3 s	31.5	32.5		
C-21	34.1 t	34.1 t	34.9 t	35.7 t	35.0	35.6	34.8 t	34.1
			35.0 t	35.7 t	35.1	35.8		
C-22	33.1 t	33.2 t	33.7 t	34.5 t	33.7	34.3	33.7 t	33.2
			33.7 t	34.5 t	33.8	34.5		
C-23	28.7 q	28.7 q	28.9 q	29.5 q	28.9	28.7	28.8 q	28.8
			29.1 q	29.8 q	29.1	28.7		
C-24	16.5 q	16.5 q	16.3 q	17.2 q	16.3	17.1	16.3 q	16.6
			16.5 q	17.3 q	16.5	17.2		
C-25	15.8 q	16.0 q	16.3 q	17.1 q	16.3	16.8	16.3 q	15.8
			16.3 q	17.2 q	16.3	17.0		
C-26	18.6 q	18.8 q	18.8 q	19.56 q	18.8	19.7	18.8 q	18.5
			18.9 q	19.64 q	18.9	19.7		
C-27	66.1 t	64.5 t	67.2 t	67.1 t	66.3	68.6	68.0 t	67.8
			67.4 t	67.6 t	67.3	68.6		
C-28	180.1 s	180.2 s	181.7 s	182.4 s	181.7	182.3	181.6 s	180.2
			181.7 s	182.5 s	181.7	182.6		
C-29	33.2 q	33.2 q	33.2 q	33.9 q	33.2	34.4	33.6 q	33.3
			33.5 q	34.2 q	33.5	34.4		
C-30	23.2 q	23.9 q	23.6 q	24.4 q	23.7	24.9	24.1 q	23.8
			23.8 q	24.9 q	23.9	24.9		

a) 100 MHz, C_5D_5N. *b*) 100 MHz, CD_3OD. *c*) 125 MHz, CD_3OD. *d*) 125 MHz, C_5D_5N.

mechanism of the formation of **2c** was considered to be the same as that of senegenin from presenegenin.[11] The lignan methyl ethers were purified after methylation with CH_2N_2 to give the dimethyl esters **2b** and **3b**, respectively. The ^{1}H-NMR spectra of these compounds were superimposable, and identical to that of dimethyl-1,2-dihydro-1-(3,4-dimethoxyphenyl)-6,7-dimethoxynaphthalene-2,3-dicarboxylate.[9a] Furthermore, the $[\alpha]_D$ values of **2b** and **3b** indicated that **3b** is an antipode of **2b**, and the positive $[\alpha]_D$ value of **2b** showed that the absolute

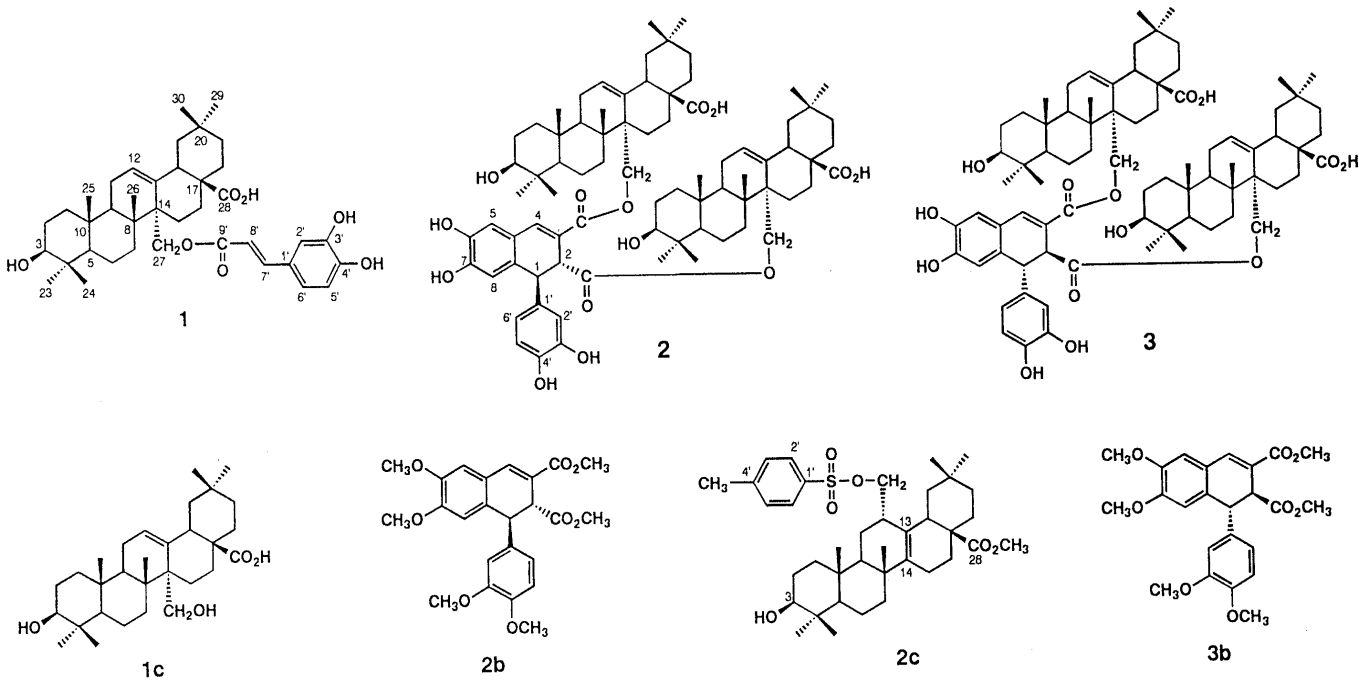


Table 2. ^{1}H-NMR Data for **2**—**7** [δ Values, J Values (Hz) in Parentheses]

	2[a]	**3**[a]	**4**[a]	**5**[b]	**6**[a]	**7**[c]
Triterpene unit						
H-3	3.13—3.21 (2H, m)	3.08 (dd, 7, 10), 3.21 (dd, 5, 11)	3.14 (dd, 5, 10), 3.20 (br t, 8)	3.10 (2H, br s)	3.13 (2H, dd, 6, 10)	3.55 (2H, dd, 6, 10)
H-18	2.68 (2H, d-like, 13)	2.82 (2H, m)	2.68 (2H, m)	2.98 (2H, m)	2.82 (2H, dd, 4, 10)	3.43 (2H, dd, 4, 13)
H-12	5.26 (t, 3), 5.45 (t, 3)	5.51 (t, 3), 5.60 (br s)	5.25 (br s), 5.45 (br s)	5.50 (br s), 5.73 (t, 3)	5.42 (2H, t, 3)	5.83 (2H, t, 3)
H-27	4.10, 4.34 (each d, 13), 4.17, 4.30 (each d, 12)	3.99, 4.40 (each d, 12), 4.13, 4.28 (each d, 13)	4.10, 4.34 (each d, 13), 4.20, 4.26 (each d, 13)	4.22 (2H, m), 4.52 (2H, m)	4.14 (2H, d, 12), 4.24 (2H, d, 12)	4.81 (2H, d, 13), 4.96 (2H, d, 13)
CH_3	0.62 (s), 0.74 (s), 0.76 (6H, s), 0.77 (s), 0.79 (s), 0.86 (s), 0.91 (6H, s), 0.95 (s), 0.96 (s), 0.99 (s)	0.57 (s), 0.71 (s), 0.75 (s), 0.78 (s), 0.79 (s), 0.80 (s), 0.81 (s), 0.90 (s), 0.91 (s), 0.96 (s), 0.98 (s), 1.01 (s)	0.61 (s), 0.74 (s), 0.758 (s), 0.763 (s), 0.77 (s), 0.79 (s), 0.84 (s), 0.90 (s), 0.91 (s), 0.95 (s), 0.96 (s), 1.00 (s)	0.65 (s), 0.72 (6H, s), 0.75 (s), 0.82 (6H, s), 0.85 (s), 0.88 (6H, s), 0.93 (s), 0.95 (s), 0.96 (s)	0.74 (6H, s), 0.75 (6H, s), 0.82 (6H, s), 0.88 (6H, s), 0.90 (6H, s), 0.94 (6H, s)	0.91 (6H, s), 0.97 (6H, s), 0.98 (6H, s), 1.03 (6H, s), 1.07 (6H, s), 1.29 (6H, s)
Phenol unit						
H-1	4.50 (br s)	4.48 (br s)	5.00 (br s)	—	—	8.43 (s)
H-2	3.82 (d, 2)	3.76 (d, 1)	3.87 (d, 1)	—	5.15, 5.16 (each d, 6)	—
H-3	—	—	—	—	3.61, 3.62 (each d, 6)	—
H-4	7.61 (s)	7.61 (s)	7.68 (s)	8.09 (s)	3.61, 3.62 (each d, 6)	8.43 (s)
H-5	6.85 (s)	6.80 (s)	6.83 (d, 8)	7.34 (d, 9)	5.15, 5.16 (each d, 6)	7.69 (s)
H-6	—	—	6.79 (d, 8)	7.28 (d, 9)	—	—
H-8	6.49 (s)	6.53 (s)	—	—	—	7.69 (s)
H-2′	6.27 (d, 2)	6.37 (d, 2)	6.32 (d, 2)	7.24 (s)	6.88 (2H, d, 2)	—
H-5′	6.62 (d, 8)	6.59 (d, 8)	6.60 (d, 8)	6.72 (s)	6.78 (2H, d, 8)	—
H-6′	6.32 (dd, 2, 8)	6.41 (dd, 2, 8)	6.37 (dd, 2, 8)	—	6.73 (2H, dd, 2, 8)	

a) 400 MHz, CD_3OD. *b*) 500 MHz, CD_3OD. *c*) 500 MHz, C_5D_5N.

configurations at C-1 and C-2 of **2b** are *S* and *R*,[9a] respectively. The locations of the ester linkages in **2** and **3** were concluded to be at the C-27 hydroxyl groups of both triterpene units, on the basis of the downfield shifts of the H-27 and C-27 signals compared with those of **1c** (Tables 1, 2). From these results, chilianthins A and B were concluded to be the diastereomeric isomers having the structures **2** and **3**, respectively.

Chilianthin C (**4**) was isolated as a white amorphous powder. The molecular formula was determined to be the same as those of **2** and **3** from positive FAB-MS (*m/z* 1267 $[M+H]^+$) and elemental analysis. The ^{1}H- and ^{13}C-NMR spectra are very similar to those of **2**, indicating the presence of two triterpene units of **1c** and a lignan moiety. In the ^{1}H-NMR spectrum, however, a couple of aromatic doublets at δ 6.79 and 6.83 (J = 8 Hz) were observed instead of two singlets in the spectrum of **2**. Considering the biogenesis of the lignan unit (*vide infra*), this spectral difference implies that the positions of the phenolic hydroxyl groups on dihydronaphthalene are C-7 and C-8. This was confirmed by a difference NOE experiment which revealed the NOE between H-4 (δ 7.68) and H-5 (δ 6.83).

Furthermore, the configurations of C-1 and C-2 were deduced from the ^{13}C-NMR data; the chemical shifts of the signals arising from the two triterpene moieties are almost superimposable on those of **2**, and slightly different from those of **3** (Table 1). This observation suggested that the absolute configurations of C-1 and C-2 are the same as those of **2**, *i.e.*, 1*S* and 2*R*, respectively. From the above evidence, the structure of chilianthin C was concluded to be as shown by the formula **4**.

Chilianthin D (**5**) was isolated as a yellow powder and was positive to the $FeCl_3$ reagent. The negative FAB-MS showed an $[M-H]^-$ ion peak at *m/z* 1261, which is 4 mass unit less than that of **4**. The ^{1}H- and ^{13}C-NMR data were related to those of **4** and indicated that **5** is also a triterpene-lignan ester having two **1c** moieties; however, the absence of the signals due to the two aliphatic methines of the dihydronaphthalene unit of **4** and the appearance of sixteen aromatic carbon signals in the ^{13}C-NMR spectrum suggested that **5** possesses an arylnaphthalene-type lignan moiety. In the aromatic region of the ^{1}H-NMR spectrum of **5**, three singlets and a pair of *ortho*-coupled doublets (δ 7.28, 7.34, $J=8$ Hz) appeared (Table 2). In the ^{1}H–^{1}H correlation spectroscopy (COSY) spectrum, weak allylic coupling (^4J) between one (δ 7.34, H-5) of the doublets and a singlet signal at δ 8.09 (H-4), and long-range (^5J) coupling between the remaining two singlets δ 6.72 (H-5′) and δ 7.24 (H-2′) were observed. Taking the results of FAB-MS into account, these observation suggested that the arylnaphthalene-type lignan unit of **5** is related to the lignan unit of **4** and has an ether ring between C-8 and C-6′.[12] This was supported by the correlations observed in the ^{1}H-detected heteronuclear multiple bond correlation (HMBC) spectrum shown in Fig. 1 and by the following chemical evidence: methylation of **5** with CH_2N_2 afforded a pentamethylate, **5a**. Subsequent hydrolysis and methylation of **5a** in a manner similar to that described for **2** and **3** yielded **2c** and a lignan methyl ester **5b** (EI-MS *m/z*: 424, M^+). The ^{1}H-NMR spectrum of **5b** showed five methyl signals due to two carboxymethyl and three aromatic methoxyl groups. The ester linkages in **5** were determined to be located at the C-27 hydroxyl groups of both triterpene units, on the basis of the downfield shifts of the H-27 and C-27 signals compared with those of **1c**. Thus, the structure **5** was assigned to chilianthin D.

Chilianthin E (**6**) was obtained as an off-white powder. The negative FAB-MS showed an $[M-H]^-$ ion peak at *m/z* 1283 which is 18 mass units larger than those of **2**, **3** and **4**, and supported the molecular formula $C_{78}H_{108}O_{15}$; however, despite the large molecular weight, only 39 carbon signals are observed in the ^{13}C-NMR spectrum.

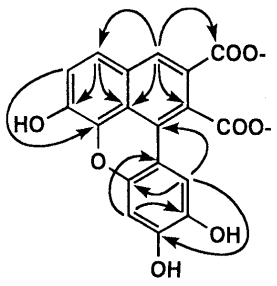
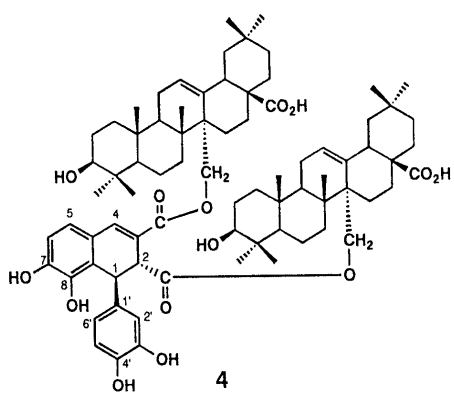


Fig. 1. HMBC Correlations (H to C) of the Lignan Moiety of **5**

This fact suggested that **6** has a symmetrical structure. The ^{1}H- and ^{13}C-NMR spectra are closely related to those of **1**, indicating the presence of triterpene **1c** units in the molecule (Tables 1, 2). Along with signals arising from the triterpene units, the ^{13}C-NMR spectrum showed signals due to ester carbonyl carbons [δ 172.3 (2C)], trisubstituted benzene rings [δ 132.4 (2C, s), 114.8 (2C, d), 146.5 (2C, s), 146.7 (2C, s), 116.3 (2C, d), 119.1 (2C, d)], and methine carbons [δ 57.9 (2C, d), δ 83.3 (2C, d)]. Dark green coloration with 2% $FeCl_3$–EtOH reagent and the appearance of ABX-type aromatic signals in the ^{1}H-NMR spectrum (Table 2) indicated that the benzene ring is a catechol-type. Furthermore, the ^{1}H–^{1}H COSY spectrum revealed vicinal coupling between the methine proton signals at δ 3.62 (H-3, 4) and 5.14 (H-2, 5). Taking the molecular weight and the symmetry of the molecule into consideration, these spectroscopic observations suggested the presence of a 2,5-bisphenyltetrahydrofuran-3,4-dicarboxylic acid moiety.[13] The nuclear Overhauser effect (NOE) correlation between H-2, 5 of the tetrahydrofuran ring and H-2′,2″ of the catechol ring also supported the structure of the proposed lignan moiety. The relative stereochemistry of this lignan moiety was determined to be 2, 3-*trans* and 3,4-*cis* on the basis of the coupling constant ($J=6$ Hz) between H-2, 5 and H-3, 4.[14] Since the signals due to H-27 and C-27 of the triterpene units were shifted to lower field compared with those of **1c**, the lignan carboxyl groups are apparently attached to these positions. On the basis of the above spectroscopic evidence, the structure of chilianthin E was concluded to be as represented by the formula **6**. Although compound **6** gave a single peak on HPLC analysis (ODS, 80% CH_3CN), the methine doublets due to H-2, 5 and H-3, 4 appeared in duplicate in the ^{1}H-NMR spectrum (Table 2). This fact suggested that **6** is a mixture of two diastereomeric isomers having enantiomeric lignan moieties.

Chilianthin F (**7**) was isolated as an off-white amorphous powder and showed a dark green coloration with 1% $FeCl_3$–EtOH reagent. Although the negative FAB-MS exhibited the $[M-H]^-$ ion peak at *m/z* 1155, the ^{1}H- and ^{13}C-NMR spectra are relatively simple compared to those of **2**, **3**, **4** and **5**, and showed signals arising from a triterpene moiety identical to that of **1** (Tables 1, 2). Besides the signals due to the triterpene units, five aromatic carbon signals [δ 111.1 (d), 127.2 (s), 128.3 (d), 130.1 (s) 151.5 (s)] and an ester carbonyl carbon signal [δ 167.9 (s)] were observed in the ^{13}C-NMR spectrum, and only two aromatic singlets [δ 8.43 (s) and 7.69 (s)] in the ^{1}H-NMR spectrum. These observations indicated that this compound also possesses a symmetrical structure. Considering the coloration of **7** with $FeCl_3$ reagent, the aromatic moiety of **7** was suggested to be a dihydroxynaphthalene dicarboxylic acid. The presence of the **1c** units and naphthalene moiety was confirmed by the following chemical evidence: methylation followed by hydrolysis with *p*-TsOH in benzene yielded **2c** and an acidic product which was subsequently methylated with CH_2N_2 to afford dimethoxynaphthalene dicarboxylic acid dimethyl ester (**7b**) (EI-MS *m/z*: 304, M^+). The substitution pattern on the naphthalene nucleus was determined by the two-dimensional NMR spectroscopic method. In the ^{1}H-



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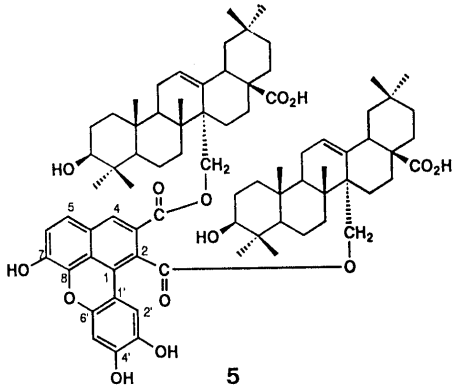

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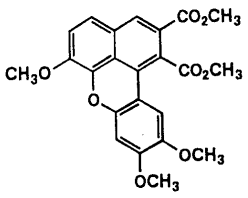
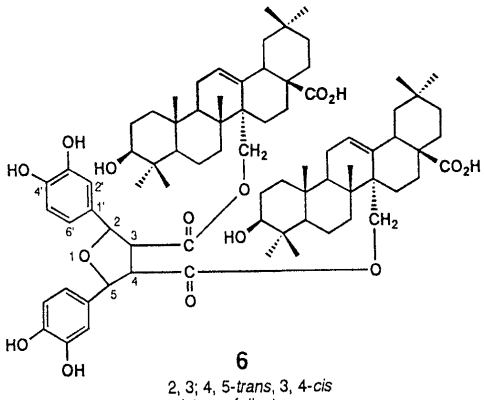
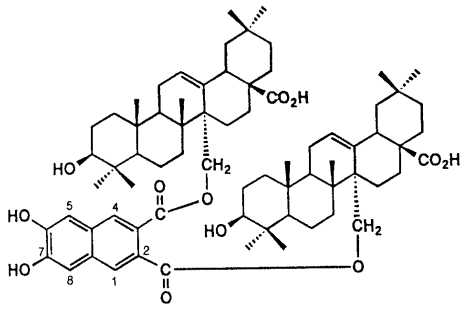


5b

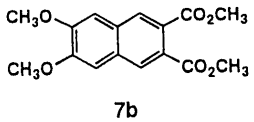


6

2, 3; 4, 5-*trans*, 3, 4-*cis*
a mixture of diastereomers



7



7b

detected heteronuclear single quantum coherence (HSQC) spectrum of **7**, the aromatic proton signals at δ 8.43 and 7.69 are correlated with the carbon signals at δ 128.3 and 111.5, respectively; while in the HMBC spectrum, the proton signal at δ 8.43 correlated with the carbon signal at δ 111.5, and the proton signal at δ 7.69 correlated with the carbon signal at δ 128.3. In addition, correlation between the proton signal at δ 8.43 and the ester carbon signal, and between the proton signal at δ 7.69 and the oxygen-bearing aromatic carbon signal (δ 151.5) indicated that the naphthalene moiety in **7** is a 6,7-dihydroxy-naphthalene 2,3-dicarboxyl group. The esters in the **1c** moieties were concluded to be at the C-27 hydroxyl groups, on the basis of the observation of an HMBC correlation between the H_2-27 signals and the ester carbonyl carbon signal. From the above spectroscopic and chemical evidence, the structure of chilianthin F was considered to be represented by the formula **7**.

To our knowledge, chilianthins A (**2**), B (**3**), C (**4**), D (**5**) and E (6) are the first example of esters consisting of two triterpene moieties and a lignan moiety. Because chilianthins are considered to be derived by oxidative coupling between two molecules of triterpene caffeate (**1**), synthesis of these compounds from **1** was attempted. Treatment of **1** with $FeCl_3$ in acetone at room temperature[9b] afforded a mixture of dimeric compounds. HPLC analysis of the mixture showed the presence of **2** and **3** as major products along with **4** and **6** as minor products. These products were separated by preparative HPLC and identified by ^{1}H-NMR comparison. Chilianthin D (**5**) is probably derived from chilianthin C (**4**) by oxidation, and chilianthin F (**7**) from **2** and **3** by oxidative elimination of the catechol ring. The possibility that these compounds are artifacts formed during storage, extraction or isolation procedure can not be ruled out, because we could not examine whether these compounds exist in the fresh bark owing to the difficulty of collection of this rare plant. However, the presence of **2** and **3** in the extract prepared only one month after collection of the bark had been ascertained, and there was no apparent change in the amounts of these compounds in the bark used in this work which had been stored for four years before extraction. Furthermore, HPLC (ODS, 70% CH_3CN) and TLC analyses showed the presence of **2**, **3**, **4** and **6** in the MeOH extract of the dried bark (stored for seven years) after extraction for only one hour at room temperature. Thus, it is unlikely that these compounds were formed during extraction or isolation. We consider that chilianthins are genuine constituents of *R. chiliantha*. The occurrence of pairs of diastereomeric compounds in this plant may suggest that the biosynthetic conversion of **1** into **2**, **3** and **6** by oxidative coupling is not enantiospecific. These characteristic metabolites could be important from the viewpoint of chemotaxonomy of the family Rhoipteleaceae.

Experimental

Optical rotations were measured with a JASCO DIP-370 digital polarimeter. ^{1}H- and ^{13}C-NMR spectra were obtained with Varian Unity plus 500, JEOL GX-400, Varian Gemini 300 and JEOL FX90Q spectrometers operating at 500, 400, 300 and 90 MHz for ^{1}H, and 125, 100 and 75 MHz for ^{13}C, respectively. Coupling constants are expressed in Hz, and chemical shifts are given on a δ (ppm) scale with tetramethylsilane as an internal standard. MS were recorded on a JEOL JMS DX-303 spectrometer, and glycerol was used as a matrix for

FAB-MS measurement. Column chromatographies were performed with Kieselgel 60 (70—230 mesh, Merck), MCI-gel CHP 20P (75—150 μm, Mitsubishi Chemical Co.), Sephadex LH-20 (25—100 μm, Pharmacia Fine Chemical Co. Ltd.), Bondapak C_{18}/Porasil B (37—75 μm, Waters Associates Inc.) and Chromatorex ODS (100—200 mesh, Fuji Silysia Chemical Ltd.). Preparative HPLC was carried out on a Tosoh apparatus equipped with a CCPM solvent delivery system, UV 8011 spectrometer (280 nm) and a TSK-GEL ODS-80TM (25 × 250 mm) column. TLC was performed on precoated Kieselgel 60 F_{254} plates (0.2 mm thick, Merck), and spots were detected by ultraviolet (UV) illumination and by spraying 1% ethanolic ferric chloride or 10% sulfuric acid reagent.

Plant Material The bark of *Rhoiptelea chiliantha* was collected in Huaping, Guangxi, China in Oct., 1988. A voucher specimen has been deposited in the Laboratory of Plant Chemotaxonomy, China Pharmaceutical University, Nanjing, China.

Extraction and Separation The air-dried ground bark (4.5 kg) was extracted with 95% EtOH to obtain an extract (570 g), which was partitioned between Et_2O (1 l) and H_2O (1 l) twice. The Et_2O layer was concentrated and treated with MeOH, then the MeOH-soluble fraction was chromatographed on MCI-gel CHP 20P (80%—100% MeOH then acetone) to afford fraction (fr.) 1 (129 g) and fr. 2 (125 g). A part of fr. 1 (53 g) was successively separated by silica gel ($CHCl_3$–MeOH–H_2O, 9 : 1 : 0.1—8 : 2 : 0.2) and Chromatorex ODS (80%—100% MeOH) column chromatographies and then preparative HPLC (MeOH–CH_3CN–H_2O, 8 : 2 : 1.8) to afford compounds **1** (7.66 g), **2** (911.6 mg), **3** (641.3 mg), **4** (9.8 mg) and **6** (26.2 mg). Remaining fr. 1 (76 g) was repeatedly chromatographed over silica gel ($CHCl_3$–MeOH–H_2O, 9 : 1 : 0.1—8 : 2 : 0.2), Chromatorex ODS (80%—100% MeOH) and Bondapak ODS (80%—90% MeOH) to afford **5** (320 mg) and **7** (116 mg), together with a mixture of **1**, **2**, **3**, **4** and **6**.

27-Caffeoyloxy-3β-hydroxyolean-12-en-28-oic Acid (1) Colorless needles (80% MeOH), mp 225—226 °C, $[\alpha]_D^{24}$ +130.9° (c=0.5, MeOH). *Anal.* Calcd for $C_{39}H_{54}O_7 \cdot H_2O$: C, 71.75; H, 8.64. Found: C, 71.44; H, 8.45. Positive ion FAB-MS m/z: 727 (M+H+glycerol)$^+$. ^{1}H-NMR (C_5D_5N, 400 MHz): 0.91, 0.92, 0.99, 1.01, 1.06, 1.20 (each 3H, s, methyl × 6), 3.39 (2H, m, H-3, 18), 4.56, 4.69 (each 1H, d, J=13 Hz, H_2-27), 5.84 (1H, br s, H-12), 6.67 (1H, d, J=16 Hz, H-8′), 7.20 (3H, s, H-2′, 5′, 6′), 7.98 (1H, d, J=16 Hz, H-7′). ^{13}C-NMR (C_5D_5N, 100 MHz): triterpene moiety see Table 1; caffeoyl moiety = 115.4 (C-8′), 115.9, 116.8 (C-2′, 5′), 121.8, (C-6′), 126.8 (C-1′), 145.7 (C-7′), 147.7 (C-3′), 150.5 (C-4′), 167.2 (C-9′).

Methylation of 1 Followed by Methanolysis A solution of **1** (300 mg) in MeOH was treated with CH_2N_2 in Et_2O to give a trimethylate **1a** (259 mg) as a white amorphous powder, $[\alpha]_D^{24}$ +119.0° (c=0.5, $CHCl_3$), positive ion FAB-MS m/z: 699 (M+Na)$^+$. ^{1}H-NMR ($CDCl_3$, 90 MHz): 0.74, 0.77, 0.84, 0.92 (×2), 0.97 (each 3H, s, methyl × 6), 2.94 (1H, dd, J=6, 13 Hz, H-18), 3.15 (1H, m, H-3), 3.65 (3H, s, –$COOCH_3$), 3.92 (6H, s, –OCH_3), 4.15, 4.35 (each 1H, d, J=13 Hz, H_2-27), 5.61 (1H, t, J=3 Hz, H-12), 6.22 (1H, d, J=16 Hz, H-8′), 6.86 (1H, d, J=8 Hz, H-5′), 7.03 (1H, d, J=2 Hz, H-2′), 7.08 (1H, dd, J=2, 8 Hz, H-6′), 7.56 (1H, d, J=16 Hz, H-7′). **1a** (80 mg) was methanolyzed by refluxing with 10% HCl in MeOH for 5 h. After evaporation *in vacuo*, the syrup was partitioned between Et_2O and water, and the organic layer was concentrated to dryness. The resulting residue was separated by silica gel chromatography with benzene–acetone (7 : 1) to afford methyl *trans*-3,4-dimethoxycinnamate (**1b**, 9 mg) as a white amorphous powder. ^{1}H-NMR ($CDCl_3$, 90 MHz): 3.80 (3H, s, –$COOCH_3$), 3.91 (6H, s, –OCH_3 × 2), 6.30 (1H, d, J=16 Hz, H-8), 6.85 (1H, d, J=8 Hz, H-5), 7.04 (1H, d, J=2 Hz, H-2), 7.11 (1H, dd, J=2, 8 Hz, H-6), 7.63 (1H, d, J=16 Hz, H-7).

Alkaline Hydrolysis of 1 A solution of **1** (300 mg) in 2.5% NaOH in H_2O–MeOH (1 : 1) (12 ml) was heated at 80 °C for 3 h. After acidification with 1% HCl, the solution was concentrated and extracted with Et_2O. The Et_2O extract was separated by silica gel chromatography with benzene–acetone (3 : 1) and then $CHCl_3$–MeOH–H_2O (9 : 1 : 0.1) to give 3β,27-dihydroxyolean-12-en-28-oic acid (**1c**, 13.3 mg) as a white powder (MeOH), mp 220—222 °C, $[\alpha]_D^{24}$ +47.1° (c=0.2, pyridine). EI-MS m/z: 472 (M$^+$), 454 (M$^+$ – H_2O), 441 (M$^+$ – CH_2OH). ^{1}H-NMR (C_5D_5N, 400 MHz): 0.89, 0.92, 1.02, 1.03, 1.05, 1.20 (each 3H, s, methyl × 6), 3.37 (1H, dd, J=5, 11 Hz, H-3), 3.40 (1H, dd, J=4, 14 Hz, H-18), 3.82, 4.09 (each 1H, d, J=13 Hz, H_2-27), 5.88 (1H, t, J=3 Hz, H-12). ^{13}C-NMR see Table 1.

Chilianthin A (2) A white amorphous powder, $[\alpha]_D^{24}$ +86.9° (c=0.5, MeOH). *Anal.* Calcd for $C_{78}H_{106}O_{14} \cdot 3H_2O$: C, 70.88; H, 8.54. Found: C, 70.67; H, 8.37. Positive ion FAB-MS m/z: 1267 (M+H)$^+$. ^{1}H-NMR data see Table 2. ^{13}C-NMR (CD_3OD, 100 MHz): triterpene moiety see Table 1; lignan moiety–47.1 (C-1), 49.9 (C-2), 116.0, 116.3, 116.9, 117.9 (C-5, 8, 2′, 5′), 119.8 (C-6′), 122.1 (C-1′), 125.6 (C-8a), 130.6 (C-3), 136.4 (C-4a), 140.4 (C-4), 144.8, 145.9, 146.1 (C-6, 3′, 4′), 149.1 (C-7), 168.4 (3-COO), 174.7 (2-COO).

Alkaline Hydrolysis of 2 A solution of **2** (12 mg) in 10% NaOH–MeOH (2 ml) was left to stand at room temperature for 12 h. After acidification with 1% HCl, the reaction solution was extracted with AcOEt, and the AcOEt extract was separated by silica gel chromatography with $CHCl_3$–MeOH–H_2O (9 : 1 : 0.1) to give **1c** (3 mg).

Methylation of 2 Followed by Hydrolysis A solution of **2** (87 mg) in MeOH was treated with CH_2N_2 in Et_2O to give a hexamethylate **2a** (76.7 mg), a part (58.1 mg) of which was hydrolyzed by refluxing with *p*-TsOH (50 mg) in benzene (5 ml) for 2 h. The reaction mixture was separated by silica gel column with benzene–acetone (7 : 1) to afford **2c** (38.1 mg) as colorless needles (benzene–hexane), mp 149—150 °C, $[\alpha]_D^{24}$ −43.7° (c=0.5, MeOH). EI-MS m/z: 640 (M$^+$), 622 (M$^+$ – H_2O), 468 (M$^+$ – TsOH). ^{1}H-NMR ($CDCl_3$, 300 MHz): 0.74, 0.78, 0.82, 0.82, 0.85, 0.94 (each 3H, s, methyl × 6), 2.46 (3H, s, Ph-CH_3), 3.11 (1H, dd, J=5, 11 Hz, H-3), 3.55 (3H, s, –$COOCH_3$), 3.79 (1H, t, J=9 Hz, –OCH_2–), 4.09 (1H, dd, J=4, 9 Hz, –OCH_2–), 7.36 (2H, d, J=8 Hz, H-2′, 6′), 7.82 (2H, d, J=8 Hz, H-3′, 5′). ^{13}C-NMR ($CDCl_3$, 75 MHz): 15.3 (q), 16.3 (q), 18.4 (t), 19.2 (q), 20.1 (t), 20.2 (t), 21.2 (t), 21.7 (q) (Ph-CH_3), 24.6 (q), 27.3 (t), 28.0 (q), 30.7 (t), 30.8 (s), 32.9 (q), 33.4 (t), 36.9 (s), 37.9 (t), 38.36 (s), 38.39 (t), 38.9 (d), 42.0 (t), 42.0 (d), 46.7 (2C, s), 51.5 (d), 51.6 (q, –$COOCH_3$), 55.3 (d), 71.7 (t, –OCH_2–), 79.0 (d, C-3), 128.0 (s, C-1′), 128.1 (2C, d, C-2′, 6′), 129.9 (2C, d, C-3′, 5′), 144.5 (×2), 144.8 (s, C-13, 14, 4′), 178.0 (s, –COO). The fractions obtained by subsequent elution of the column with $CHCl_3$–MeOH–H_2O (9 : 1 : 0.1) were treated with CH_2N_2 in Et_2O. Purification of the product by silica gel chromatography (benzene–acetone) gave **2b** (8.8 mg) as a white amorphous powder, $[\alpha]_D^{24}$ +146.8° (c=0.3, $CHCl_3$). EI-MS m/z: 442 (M$^+$). ^{1}H-NMR (acetone-d_6, 90 MHz): 3.58, 3.70, 3.72 (×2), 3.78, 3.86 (each 3H, s, –OCH_3 × 6), 3.97 (1H, d, J=2 Hz, H-2), 4.64 (1H, d, J=2 Hz, H-1), 6.43 (1H, dd, J=2, 8 Hz, H-6′), 6.75 (1H, d, J=8 Hz, H-5′), 6.77 (1H, d, J=2 Hz, H-2′), 6.84 (1H, s, H-8), 7.11 (1H, s, H-5), 7.67 (1H, s, H-4). ^{1}H-NMR ($CDCl_3$, 90 MHz): 3.64, 3.75, 3.79, 3.80, 3.82, 3.91 (each 3H, s, –OCH_3 × 6), 3.99 (1H, d, J=3 Hz, H-2), 4.65 (1H, d, J=3 Hz, H-1), 6.43 (1H, dd, J=2, 8 Hz, H-6′), 6.64 (1H, d, J=2 Hz, H-2′), 6.66 (1H, s, H-8), 6.68 (1H, d, J=8 Hz, H-5′), 6.87 (1H, s, H-5), 7.66 (1H, s, H-4). ^{13}C-NMR ($CDCl_3$, 100 MHz): 45.7 (C-1), 47.3 (C-2), 51.9, 52.5 (–$COOCH_3$), 58.9 (2C), 56.0, 56.1 (-OCH_3), 111.0, 111.2, 111.8, 112.2 (C-5, 8, 2′, 5′), 119.8 (C-6′), 122.6 (C-1′), 124.3 (C-8a), 130.3 (C-3), 135.0 (C-4a), 137.5 (C-4), 148.0, 148.3, 149.0 (C-6, 3′, 4′), 150.9 (C-7), 167.0 (3-COO), 172.9 (2-COO).

Chilianthin B (3) A white amorphous powder, $[\alpha]_D^{24}$ +49.4° (c=0.5, MeOH). *Anal.* Calcd for $C_{78}H_{106}O_{14} \cdot 3H_2O$: C, 70.88; H, 8.54. Found: C, 70.45; H, 8.32. Positive ion FAB-MS m/z: 1267 (M+H)$^+$. ^{1}H-NMR data see Table 2. ^{13}C-NMR (CD_3OD, 100 MHz): triterpene moiety see Table 1; lignan moiety–47.4 (C-1), 50.5 (C-2), 116.5, 117.0, 117.9, 118.3 (C-5, 8, 2′, 5′), 120.4 (C-6′), 123.7 (C-1′), 125.9 (C-8a), 131.9 (C-3), 137.6 (C-4a), 140.8 (C-4), 145.8, 146.8, 147.0 (C-6, 3′, 4′), 150.1 (C-7), 169.3 (3-COO), 174.4 (2-COO).

Alkaline Hydrolysis of 3 **3** (20 mg) was hydrolyzed with 10% NaOH–MeOH in a manner similar to that described for **2** to furnish **1c** (5 mg).

Methylation of 3 Followed by Hydrolysis A solution of **3** (200 mg) in MeOH was treated with CH_2N_2 in Et_2O to give a hexamethylate **3a** (135.6 mg), a part (106.0 mg) of which was hydrolyzed by refluxing with *p*-TsOH (100 mg) in benzene (10 ml) for 4 h. Work-up in a manner similar to that described for **2** afforded **2c** (27.0 mg) and **3b** (14 mg). **3b**: a white amorphous powder, $[\alpha]_D^{24}$ −72.9° (c=0.3, $CHCl_3$). EI-MS m/z: 442 (M$^+$). ^{1}H-NMR (acetone-d_6, 90 MHz): identical to that of **2b**.

Chilianthin C (4) A white amorphous powder, $[\alpha]_D^{20}$ +60.8° (c=0.3, MeOH). *Anal.* Calcd for $C_{78}H_{106}O_{14} \cdot 6H_2O$: C, 68.10; H, 8.64. Found: C, 68.49; H, 8.53. Positive ion FAB-MS m/z: 1267 (M+H)$^+$. ^{1}H-NMR data see Table 2. ^{13}C-NMR (CD_3OD, 100 MHz): triterpene moiety see Table 1; lignan moiety–(signal due to C-1 was overlapped with solvent peak), 47.0 (C-2), 114.6 (C-6), 115.9, 116.3 (C-2′, 5′), 119.9 (C-6′), 121.7 (C-1′), 122.6 (C-5), 124.9, 126.2 (C-4a, 8a), 135.6 (C-3), 141.1 (C-4), 144.3, 144.6, 145.9 (C-7, 3′, 4′), 149.1 (C-8), 168.4 (3-COO), 174.7 (2-COO).

Chilianthin D (5) A yellow amorphous powder, $[\alpha]_D^{24}$ +14.3° (c=0.4,

MeOH). *Anal.* Calcd for $C_{78}H_{102}O_{14}\cdot 4H_2O$: C, 70.14; H, 8.30. Found: C, 70.02; H, 7.78. Negative ion FAB-MS *m/z*: 1261 $(M-H)^-$. ^{1}H-NMR data see Table 2. ^{13}C-NMR (CD_3OD, 125 MHz): triterpene moiety see Table 1; lignan moiety–106.0 (C-5′), 111.8 (C-1′), 113.2 (C-2′), 121.8 (C-6), 122.7 (C-5), 122.9 (C-2), 125.5 (C-8a), 126.5 (2C, C-1, 3), 128.8 (C-4a), 130.7 (C-4), 139.3 (C-8), 144.0, 144.1 (C-3′, 7), 148.9 (C-4′), 150.5 (C-6′), 167.5 (3-COO), 174.0 (2-COO).

Methylation of 5 Followed by Hydrolysis A solution of **5** (39 mg) in MeOH was treated with CH_2N_2 in Et_2O to give a pentamethylate **5a** (32.6 mg) as a light yellow amorphous powder, $[\alpha]_D^{15}$ +83.0° (*c*=0.1, $CHCl_3$). Negative ion FAB-MS *m/z*: 1331 $(M-H)^-$. ^{1}H-NMR ($CDCl_3$, 300 MHz): triterpene moiety–0.60, 0.69, 0.78 (×2), 0.79 (×2), 0.83 (×2), 0.90 (×2), 0.94, 0.97 (each 3H, s, methyl×12), 3.03 (2H, m, H-18, 18′), 3.18 (2H, m, H-3, 3′), 3.59, 3.68 (each 3H, s, $-COOCH_3\times 2$), 4.22, 4.40 (each 2H, d, *J*=13 Hz, H_2-27, H_2-27′), 5.48, 5.76 (each 1H, t, *J*=2 Hz, H-12, 12′); lignan moiety–3.92 (×2), 4.06 (each 3H, s, $-OCH_3\times 3$), 6.80 (1H, s, H-5′), 7.26 (1H, s, H-2′), 7.37 (1H, d, *J*=9 Hz, H-6), 7.41 (1H, d, *J*=9 Hz, H-5), 8.14 (1H, s, H-4). **5a** (30 mg) was hydrolyzed by refluxing with *p*-TsOH (30 mg) in benzene (6 ml) for 3 h. Work-up similar to that described for **2** gave **2c** (10 mg) and **5b** (3 mg): a yellow amorphous powder, HR-EI-MS *m/z*: 424.1156 (M^+) (Calcd for $C_{23}H_{20}O_8$: 424.1158). ^{1}H-NMR ($CDCl_3$, 300 MHz): 3.90, 3.93 (×2) (each 3H, s, $-OCH_3\times 3$), 4.05, 4.06 (each, 3H, s, $-COOCH_3\times 2$), 6.80 (1H, s, H-5′), 7.26 (1H, s, H-2′), 7.37 (1H, d, *J*=9 Hz, H-6), 7.41 (1H, d, *J*=9 Hz, H-5), 8.14 (1H, s, H-4).

Chilianthin E (6) A white amorphous powder, $[\alpha]_D^{15}$ +97.1° (*c*=1, MeOH). *Anal.* Calcd for $C_{78}H_{108}O_{15}\cdot 7.5H_2O$: C, 65.94; H, 8.73. Found: C, 65.68; H, 7.94. Negative ion FAB-MS *m/z*: 1283 $(M-H)^-$. ^{1}H-NMR data see Table 2. ^{13}C-NMR (CD_3OD, 100 MHz): triterpene moiety see Table 1; lignan moiety: 57.9 (C-3, 4), 83.3 (C-2, 5), 114.8 (2C, C-2′), 116.3 (2C, C-5′), 119.1 (2C, C-6′), 132.4 (2C, C-1′), 146.5, 146.7 (each 2C, C-3′, 4′), 172.3 (2C, 3, 4-COO).

Chilianthin F (7) A white amorphous powder, $[\alpha]_D^{24}$ +96.3° (*c*=0.4, MeOH). *Anal.* Calcd for $C_{72}H_{100}O_{12}\cdot 5H_2O$: C, 69.31; H, 8.89. Found: C, 68.98; H, 8.50. Negative ion FAB-MS *m/z*: 1155 $(M-H)^-$. ^{1}H-NMR data see Table 2. ^{13}C-NMR (CD_3OD, 125 MHz): triterpene moiety see Table 1; naphthalene carboxylic acid moiety: 111.1 (C-5, 8), 127.2 (C-2, 3), 128.3 (C-1, 4), 130.1 (C-4a, 8a), 151.5 (C-6, 7), 167.9 (2, 3-COO).

Methylation of 7 Followed by Hydrolysis A solution of **7** (106 mg) in MeOH was treated with CH_2N_2 in Et_2O to give a tetramethylate **7a** (66 mg) as a white amorphous powder, $[\alpha]_D^{15}$ +73.3° (*c*=1.0, $CHCl_3$). Positive ion FAB-MS *m/z*: 1235 $(M+Na)^+$. ^{1}H-NMR ($CDCl_3$, 300 MHz): triterpene moiety–0.74, 0.77, 0.83, 0.90, 0.91, 0.97 (each 6H, s, methyl×6), 2.98 (2H, m, H-18), 3.20 (2H, m, H-3), 3.65 (6H, s, $-COOCH_3$), 4.35, 4.52 (each 2H, d, *J*=12 Hz, H_2-27), 5.61 (2H, t, *J*=3 Hz, H-12); naphthalene carboxylic acid moiety–4.04 (6H, s, $-OCH_3$), 7.11 (2H, s, H-5, 8), 8.00 (2H, s, H-1, 4). 7a (54 mg) was hydrolyzed by refluxing with *p*-TsOH (50 mg) in benzene (10 ml) for 4 h. Work-up in a manner similar to that described for **2** yielded **2c** (15 mg) and **7b** (6 mg). **7b**: a white amorphous powder, HR-EI-MS *m/z*: 304.0941 (Calcd for $C_{16}H_{16}O_6$: 304.0947). ^{1}H-NMR ($CDCl_3$, 300 MHz): 3.95, 4.04 (each 6H, s, $-COOCH_3\times 2$, $-OCH_3\times 2$), 7.51 (2H, s, H-5, 8), 8.12 (2H, s, H-1, 4).

Synthesis of 2, 3, 4 and 6 from 1 A solution of **1** (1 g) and anhydrous $FeCl_3$ (500 mg) in 97% acetone was left to stand at room temperature for 1 h. After acidification with 1% HCl (10 ml), the reaction mixture was concentrated and partitioned between Et_2O and water. The Et_2O layer was dried over Na_2SO_4, concentrated, and eluted from a silica gel column with $CHCl_3$–MeOH–H_2O (9:1:0.1) to give a mixture of dimeric compounds (318.2 mg) along with recovery of the starting material (**1**, 365.8 mg). A part of the dimer fraction (200 mg) was separated by preparative HPLC (ODS, MeOH–CH_3CN–H_2O, 8:2:1.8) to give **2** (25 mg), **3** (36 mg), **4** (4.8 mg) and **6** (4.2 mg).

Acknowledgment This work was supported by a Grant-in-Aid for Scientific Research (No. 07672273) from the Ministry of Education, Science, Sports and Culture of Japan, and by a Yamamura Yuichi Memorial WAKAN-YAKU Research Grant. We thank Mr. K. Inada, Y. Ohama and Mr. N. Yamaguchi (Nagasaki University) for obtaining NMR and MS data. One of the authors (Z. Jiang) is grateful to the Japanese Government for the award of a scholarship.

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