New Sesquiterpenes from *Chloranthus japonicus*

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Chemical investigation of the roots of *Chloranthus japonicus* SIEB. has resulted in the isolation and characterization of four new eudesmane-type sesquiterpenes including two new sesquiterpene cinnamates, along with one new and two known sesquiterpene dimers. Their structures were established by spectroscopic means and by comparison with the respective literature values.

Introduction. – *Chloranthus japonicus* SIEB., with the Chinese name 'Yinxiancao', belonging to the family Chloranthaceae, has long been used in folk medicine in China [1]. Previous chemical investigations of this plant resulted in the isolation of various compounds including eudesmane-type sesquiterpenes [2][3], lindenane-type sesquiterpenes [2–6], germacrane-type sesquiterpenes [3][5], acorane-type sesquiterpenes [3], lindenane-type sesquiterpene dimers and trimers [7–10], some of which were reported to inhibit the expression of cell adhesion molecules [11][12]. During the present search for biologically active substances, we isolated four eudesmane-type sesquiterpenes, namely 5α-(cinnamoyloxy)-8,12-epoxy-3-methoxy-7βH,8αH-eudesma-3,11-dien-6-one (**1**) and 8β-(cinnamoyloxy)eudesma-4(14),7(11)-dien-12,8-olide (**2**), 8,12-epoxy-1α-hydroxy-4αH,5αH-eudesma-7,11-diene-6,9-dione (**3**), and 8,12-epoxy-1α-methoxy-4αH,5αH-eudesma-7,11-diene-6,9-dione (**4**), along with one new sesquiterpene dimer **5**, named yinxiancaol, and two known compounds, shizukaol B (**6**) and shizukaol E (**7**).

Results and Discussion. – Compound **1** was obtained as a yellowish optically active oil. The HR-FT-ICR-MS exhibited a molecular ion peak at m/z 431.1830 ($[M+\mathrm{Na}]^+$; calc. 431.1834), indicating the molecular formula $C_{25}H_{28}O_5$. The IR spectrum revealed the presence of an aromatic ring and two C=O groups, characterized by absorptions at $\tilde{\nu}_{max}$ 1604, 1508, 1355, 1720, and 1714 cm^{-1}, respectively. Comparison of the ^{1}H- and ^{13}C-NMR data of **1** with those of eudesmane-type sesquiterpenes established the presence of the same backbone with one MeO and one ketone group in the molecule of **1** [13][14]. The C-atom signal at δ 169.3 in the ^{13}C-NMR spectrum was attributable to the C=O of a cinnamoyl group, whose (E)-configuration was inferred from a large coupling constant of 16.2 Hz between the two olefinic H-atoms at δ 8.09 (d, $J = 16.2$) and 6.95 (d, $J = 16.2$) [15]. Apart from one C=O group and one oxygenated olefinic C-atom, there were two oxygenated C-atoms in the molecule, one of which was linked with the cinnamoyl group. Due to the long-range correlations observed from the H-

atom signals at δ 1.63 (*s*, Me(15)[1])), 1.61–1.65 (*m*, H_α–C(1)), 2.05–2.09 (*m*, H_β–C(1)), 2.18–2.23 (*m*, H_α–C(9)), and 2.03–2.07 (*m*, H_β–C(9)) to the C-atom signal at δ 88.1 (*s*, C(5)) in the HMBC spectrum, C(5) was inferred to be oxygenated. Correlations from the olefinic H-atom signal at δ 7.65 (*s*, H–C(12), 1 H) to the C-atom signal at δ 77.2 (*d*, C(8)) indicated that C(8) and C(12) were connected *via* an O-atom. Thus, the cinnamoyloxy group was inferred to be located at C(5). The observation of HMBC correlations from the H-atom signals at δ 1.61–1.65 (*m*, H_α–C(1)) and 2.05–2.09 (*m*, H_β–C(1)) to the C-atom signal at δ 150.3 (*s*, C(3)), and correlations from the H-atom signal at δ 1.83 (*s*, Me(14)) to the C-atom signals at δ 150.3 (*s*, C(3)) and 135.9 (*s*, C(4)) suggested that a C=C bond was located between C(3) with C(4). The MeO group was at C(3) due to the HMBC correlation from the MeO signal at δ(H) 3.99 (*s*) to the C-atom signal at δ 150.3 (*s*, C(3)). The relative configuration of **1** was determined on the basis of the NOESY spectrum and analysis of the coupling constants as follows: the large coupling constant of the H-atom signal at δ 2.86 (*d*, J = 12.3 Hz, H–C(7)) indicated that rings *B* and *C* are *trans*-fused. The observation of NOESY

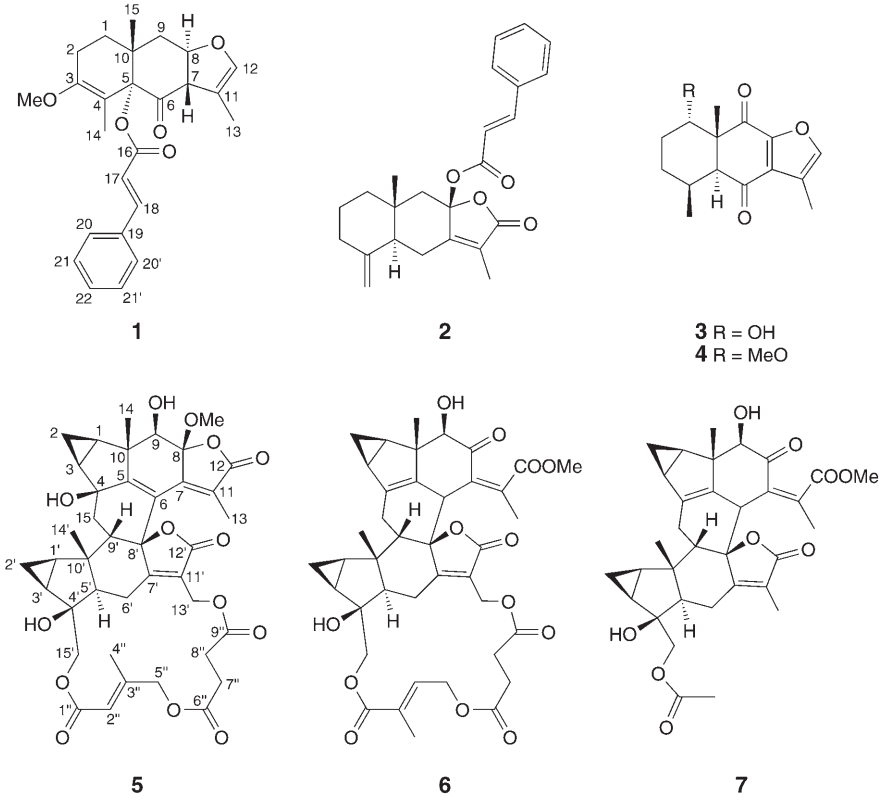

Figure. *The structures of* **1**–**7**

[1]) Arbitrary numbering; see the *Figure*.

correlations between the H-atom signal at δ 2.86 (d, J = 12.3 Hz, H–C(7)) and the H-atom signals at δ 1.63 (s, Me(15)) and 2.03–2.07 (m, H_β–C(9)) revealed that H–C(7) was in a β-configuration as shown in the *Figure.* Compound **1** was thus elucidated as 5α-(cinnamoyloxy)-8,12-epoxy-3-methoxy-7βH,8αH-eudesma-3,11-dien-6-one with as yet undetermined absolute configuration. The complete ^{1}H- and ^{13}C-NMR signal assignments are listed in *Table 1*.

Table 1. *NMR Spectral Data for* **1** *and* **2**[1]). δ in ppm, J in Hz.

Position	**1**[a])		**2**[b])	
	δ(H)[c])	δ(C)[d])	δ(H)[c])	δ(C)[d])
1α	1.61–1.65 (m)	33.6 (t)	1.25–1.28 (m)	41.6 (t)
1β	2.05–2.09 (overlapped)		1.50–1.55 (m)	
2α	2.24–2.27 (m)	24.8 (t)	1.56–1.58 (m)	21.4 (t)
2β	2.05–2.09 (overlapped)		1.56–1.58 (m)	
3α		150.3 (s)	1.88–1.92 (m)	35.5 (t)
3β			2.28–2.31 (m)	
4		135.9 (s)		149.1 (s)
5		88.1 (s)	1.91–1.93 (m)	50.3 (d)
6α		201.8 (s)	2.60–2.65 (m)	22.8 (t)
6β			2.23–2.26 (m)	
7β	2.86 (d, J = 12.3)	63.8 (d)		162.5 (s)
8α	3.46–3.49 (m)	77.2 (d)		104.2 (s)
9α	2.18–2.23 (m)	37.5 (t)	1.45 (d, J = 14.3)	51.7 (t)
9β	2.03–2.07 (m)		2.12 (d, J = 14.3)	
10		41.3 (s)		37.5 (s)
11		123.1 (s)		121.1 (s)
12	7.65 (s)	145.9 (d)		170.9 (s)
13	2.23 (s)	9.9 (q)	1.75 (s)	8.1 (q)
14	1.83 (s)	24.8 (q)	4.85, 4.63 (2s)	106.5 (t)
15	1.63 (s)	22.8 (q)	0.93 (s)	17.2 (q)
16		169.3 (s)		166.9 (s)
17	8.09 (d, J = 16.2)	144.1 (d)	7.61 (d, J = 16.0)	144.5 (d)
18	6.95 (d, J = 16.2)	121.0 (d)	6.30 (d, J = 16.0)	118.6 (d)
19		135.1 (s)		134.6 (s)
20	7.35–7.38 (m)	129.3 (d)	7.34–7.38 (m)	130.6 (d)
21	7.63–7.66 (m)	128.5 (d)	7.43–7.47 (m)	130.2 (d)
22	7.34–7.38 (m)	130.3 (d)	7.28–7.32 (m)	128.6 (d)
MeO	3.99 (s)	54.5 (q)		

[a]) Recorded in (D_5)pyridine. [b]) Recorded in (D_6)DMSO. [c]) Recorded at 500 MHz. [d]) Recorded at 125 MHz, multiplicities inferred from DEPT and HMQC experiments.

Compound **2** was obtained as a yellowish optically active oil. The HR-FT-ICR-MS exhibited a ion peak at m/z 401.1725 ($[M+Na]^+$; calc. 401.1729). The molecular formula was determined to be $C_{24}H_{26}O_4$ with the aid of ^{1}H- and ^{13}C-NMR data. The main part of the structure highly resembles the known eudesmane-type sesquiterpene 8β-hydroxyeudesma-4(14),7(11)-dien-12,8-olide [16] by comparison of the ^{1}H- and ^{13}C-NMR data. The C-atom signals at 166.9 (s), 144.5 (d), 118.6 (d), 134.6 (s), 130.6

(*d*), 130.2 (*d*), and 128.6 (*d*) are characteristic for a cinnamoyloxy group in the molecule [15]. C(8)[1]) is the only position where the cinnamoyloxy group can be located. Compound **2** was thus elucidated as 8β-(cinnamoyloxy)eudesma-4(14),7(11)-dien-12,8-olide with as yet undetermined absolute configuration. The assignments of individual H-atoms and C-atoms were made by ^{1}H,^{1}H-COSY, HMQC, and HMBC spectroscopy. The complete ^{1}H- and ^{13}C-NMR signal assignments are listed in *Table 1*.

Compound **3** was obtained as a yellowish, optically active oil. The HR-FT-ICR-MS exhibited a ion peak at *m*/*z* 285.1095 ($[M+Na]^+$; calc. 285.1103). The molecular formula was determined to be $C_{15}H_{18}O_4$ with the aid of ^{1}H- and ^{13}C-NMR data. Comparison of the ^{1}H- and ^{13}C-NMR data of **3** with compounds **1**, **2**, and those of eudesmane-type sesquiterpenes established the presence of the same backbone [13][14]. The signal at δ 7.43 (*Table 2*) was characteristic of H–C(12) in 8,12-epoxyeudesma-7,11-diene sesquiterpenes [14]. The two CO signals at δ 185.5 and 192.0 indicated the presence of two α,β-unsaturated keto groups. The OH group was located at C(1)[1]) (*s*, δ 68.2) based on the observed long-range correlations between the H-atom signal at δ 3.61 (*dd*, J = 6.0, 2.0, H_β–C(1)) and the C-atom signals at δ 54.1 (*s*, C(10)), 12.1 (*q*, C(15)), 26.6 (*t*, C(3)), and 49.7 (*s*, C(5)) in the HMBC spectrum. The relative configuration of **3** was determined on the basis of the NOESY data and coupling-constant analysis. H–C(1) was assigned as equatorially oriented according to the observed coupling constants (3.61, *dd*, J = 6.0, 2.0). Thus H–C(1) was assigned as being β-oriented, and the OH-group at C(1) was in the α-position as shown in the *Figure*. The coupling constant for H_α–C(5) (2.81, *d*, J = 6.0) revealed that H–C(4) was equatorially oriented. Thus, the H–C(4) was determined to be α-oriented, while the Me(14) group was in the β-position, which was confirmed by the NOESY correlation between the H-atom signal at δ 2.25 (*s*, Me(15)) to the H-atom signal at δ 1.15 (*d*, J = 7.5 Hz, Me(14)). Compound **3** was thus elucidated as 8,12-epoxy-1α-hydroxy-4αH,5αH-eudesma-7,11-diene-6,9-dione with as yet undetermined absolute configuration.

Compound **4** was obtained as a yellowish, optically active oil, and the HR-FT-ICR-MS exhibited a molecular ion peak at *m*/*z* 251.1436 ($[M+H]^+$; calc. 277.1440), corresponding to the molecular formula $C_{16}H_{20}O_4$. Besides, there was a MeO signal in **4**, and the ^{1}H- and ^{13}C-NMR spectra of **4** (*Table 2*) showed similar chemical shifts and the same multiplicity for most of the H- and C-atoms as for **3**, indicating that **4** is the *O*-methylated derivative of **3**. This was confirmed by HMBC and NOESY experiments. Compound **4** was thus elucidated as 8,12-epoxy-1α-methoxy-4αH,5αH-eudesma-7,11-diene-6,9-dione with as yet undetermined absolute configuration.

Compound **5** was obtained as an amorphous powder. The HR-FT-ICR-MS exhibited a molecular ion peak at *m*/*z* 771.2627 ($[M+Na]^+$; calc. 771.2623), corresponding to the molecular formula $C_{40}H_{44}O_{14}$, which indicated 19 degrees of unsaturation. The IR spectrum revealed the presence of OH groups and α,β-unsaturated butyrolactone and ester groups, characterized by absorptions at $\tilde{\nu}_{max}$ 3448, 1766, and 1730 cm^{-1}. In the ^{1}H-NMR spectrum in (D_6)DMSO, 44 H-atom signals were observed, among which three *singlets* at δ 5.33, 4.82 and 4.48 (disappearing when exchanged with D_2O). Two strongly shielded CH_2 groups (δ 0.83 (*ddd*, J = 8.5, 8.5, 3.0) and 1.05–1.09 (*m*); δ 0.62 (*ddd*, J = 8.5, 8.5, 4.5) and 1.21–1.25 (*m*)) indicated the presence of two cyclopropane rings, confirmed by two pairs of four-H-atom spin

Table 2. *NMR Spectral Data for* **3** *and* **4**[1]). δ in ppm, J in Hz.

Position	**3**[a])		**4**[a])	
	δ(H)[b])	δ(C)[c])	δ(H)[b])	δ(C)[c])
1β	3.61 (*dd*, J = 6.0, 2.0)	68.2 (*d*)	3.61 (*dd*, J = 6.5, 2.5)	70.4 (*d*)
2α	2.77–1.79 (*m*)	40.1 (*t*)	2.80–2.84 (*m*)	40.6 (*t*)
2β	2.55–2.59 (*m*)		2.55–2.59 (*m*)	
3α	1.68–1.72 (overlapped)	26.6 (*t*)	1.70–1.74 (overlapped)	26.0 (*t*)
3β	1.68–1.72 (overlapped)		1.70–1.74 (overlapped)	
4	1.79–1.82 (*m*)	45.2 (*d*)	1.77–1.81 (*m*)	46.1 (*d*)
5α	2.81 (*d*, J = 6.0)	49.7 (*d*)	2.79–2.82 (*m*)	50.30 (*d*)
6		185.5 (*s*)		185.8 (*s*)
7		133.6 (*s*)		133.6 (*s*)
8		163.2 (*s*)		162.2 (*s*)
9		192.0 (*s*)		193.4 (*s*)
10		54.1 (*s*)		53.7 (*t*)
11		124.1 (*s*)		124.6 (*s*)
12	7.43 (*s*)	144.5 (*s*)	7.48 (*s*)	144.7 (*s*)
13	2.30 (*s*)	9.9 (*q*)	2.31 (*s*)	10.2 (*q*)
14	1.15 (*d*, J = 7.5)	17.8 (*q*)	1.13 (*d*, J = 7.3)	17.2 (*q*)
15	2.25 (*s*)	12.1 (*q*)	2.28 (*s*)	12.0 (*q*)
MeO			3.42(*s*)	52.6 (*q*)

[a]) Recorded in (D_6)DMSO. [b]) Recorded at 500 MHz. [c]) Recorded at 125 MHz, multiplicities inferred from DEPT and HMQC experiments.

systems at δ 1.55–1.57 (*m*), 0.83 (*ddd*, J = 8.5, 8.5, 3.0 Hz), 1.05–1.09 (*m*), 1.73–1.78 (*m*), and at δ 1.65–1.69 (*m*), 0.62 (*ddd*, J = 8.5, 8.5, 4.5 Hz), 1.21–1.25 (*m*), and 1.45–1.48 (*m*) in the ^{1}H,^{1}H-COSY spectra. The ^{13}C-NMR spectrum in (D_6)DMSO (*Table 3*) contained 40 C-atom signals, consisting of five CO-groups, four C=C bonds, five Me groups, nine CH_2 groups, seven H–C groups, and six quaternary C-atoms. The high-field region of the ^{13}C-NMR spectrum of **5** showed a Me signal at δ 10.2 (*q*) characteristic of Me(13)[1]) in the lindenane sesquiterpene lactones [2][17]. Two upfield methylene signals at δ 9.04 (*t*) and 10.5 (*t*) also indicated the presence of two three-membered rings [2][17]. These data strongly suggest that there are two lindenane units in the molecule of **5**. Natural lindenane sesquiterpene dimers were reported to be connected between C(15)–C(9′) and C(6)–C(8′) [7][9][10][18–20]. The characteristic ^{13}C-NMR signals at δ 41.7 (*t*, C(15)), 87.0 (*s*, C(8′)), and 52.1 (*d*, C(9′)) revealed that two lindenane units of compound **5** were dimerized in the same manner as noted previously for chloramultilide A and shizukaols A–I [9][18]. The gross structure of **5** was determined by 2D-NMR including HMQC and HMBC experiments. The H-atom signal at δ 3.85 (*s*, H–C(9)) and a MeO signal at δ 3.45 (*s*, MeO) exhibited HMBC correlations with the dioxygenated quaternary C-atom signal at δ 104.9 (*s*, C(8)), indicating that the only MeO group is located at C(8), and a five-membered lactone ring is formed between C(8) and C(12). The observation of long-range correlations between the H-atom signals at δ 4.53 (*d*, J = 12.0 Hz, H_a–(13′)), 4.90 (*d*, J = 12.0 Hz, H_b–C(13′)), 2.43 (*dd*, J = 12.0, 7.5 Hz, H–C(5′)), and the strongly deshielded olefinic C-atom signal at δ 174.8 (*s*) hinted that C(7′) was deshielded by a macrocyclic ring in

the molecule [9][18]. The ester CO group signals at δ 166.9 (*s*), 171.7 (*s*), and 172.3 (*s*) confirmed the presence of a macrocyclic tris-lactone unit. The oxygenated CH_2 signals at δ 54.2 (*t*, C(13′)) and 73.5 (*t*, C(15′)) suggested that this ring was likely to be attached at C(13′) and C(15′). This inference was further confirmed by the observation of HMBC correlations of CH_2(13′)/C(7′), CH_2(13′)/C(9″), CH_2(15′)/C(5′), and CH_2(15′)/C(1″). Such macrocyclic ester rings were reported to be constructed by a C_5-hydroxy acid, and γ-hydroxy acid or γ-hydroxysenecioic acid, and a C_4-dicarboxylic acid, succinic or malic acid, as determined by heteronuclear NOE experiments [18–21]. An olefinic H-atom signal was observed as a *singlet* in a relatively upfield region at δ 5.89 (*s*) in the ^{1}H-NMR spectrum of **5** indicating that the macrocyclic lactone ring has a γ-hydroxysenecioic acid moiety (–O–CH_2–C(Me)=CH–CO–). This was confirmed by HMBC correlations between the Me signal at δ 2.12 (*s*, Me(4″)) and the signal for the oxygenated CH_2 group at δ 65.8 (*t*, C(5″)) [9]. The NOESY correlation of H–C(2″) with CH_2(5″) indicated (*E*)-configuration of the double bond within the γ-hydroxysenecioic acid moiety. Another residue of the lactone ring was deduced to be a succinyl unit from the HMBC correlation of CH_2(7″) and CH_2(8″) to the two ester CO groups CO(6″) and CO(9″). The stereochemical relationship between the rings and the two lindenane sesquiterpene units was determined by a 2D-NOESY experiment and by comparison with literature values [18]. The observation of a NOESY correlation between H–C(9) and H–C(5′), characteristic for lindenane sesquiterpene dimers connected at C(15)–C(9′) and C(6)–C(8′), suggested that the molecule is folded back at the six-membered ring between two sesquiterpene units [9][18]. The relative configuration of C(8) is deduced by the NOESY correlation from the MeO H-atoms to Me(14), indicating that the MeO and Me(14) groups are on the same side of the molecule. From the foregoing data, **5** (*Fig.*) was determined to be a new lindenane sesquiterpene dimer and was given the trivial name yinxiancaol. The complete ^{1}H- and ^{13}C-NMR signal assignments are listed in *Table 3*.

Furthermore, two known lindenane-type sesquiterpene dimers, shizukaol B (**6**) and shizukaol E (**7**) were identified by comparison of their spectroscopic data with reference values [9][20].

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Experimental Part

General. TLC: *Merck* precoated plates (silica gel *60 F254*) of 0.25-mm thickness. Chromatography: *Waters 600* prep. HPLC, with a *Shim-pack PREP-ODS* (250 × 20 mm) column; *Sephadex LH-20* (*Amersham*). M.p. (uncorrected): *Reichert* apparatus. Optical rotations: *Perkin-Elmer 341* polarimeter. IR Spectra: *Nicolet Avatar-360* FT-IR spectrometer. ^{1}H-NMR (500 MHz) and ^{13}C-NMR (125 MHz) spectra: *Bruker AVANCE DMX-500* NMR spectrometer with TMS as internal standard (at 25°). ESI-MS: *Bruker Esquire-3000^{plus}* spectrometer. HR-FT-ICR-MS: *Bruker Apex III* spectrometer.

Plant Material. The leaves and stem of *C. japonicus* SIEB. were collected in Zhejiang Province, China, in September 2004 and identified by Prof. *Changxi Zhang* (Jinhua Medical College, Jinhua, P. R. China). A voucher specimen (No. zju 6995) is kept in College of Agriculture and Biotechnology, Zhejiang University, Hangzhou, P. R. China.

Extraction and Isolation. The shade-dried leaves and stem (2 kg) were extracted with MeOH, and 54 g extract was obtained, which was partitioned with petroleum ether (PE), AcOEt, and BuOH successively. The PE extract (16 g) was subjected to column chromatography (CC) (800 g SiO_2, 200–300

Table 3. *NMR Spectral Data for* **5**[a]). δ in ppm, J in Hz.

Position	δ(H)[b])	δ(C)[c])	^{1}H,^{1}H-COSY	HMBC[d])
1	1.55–1.57 (*m*)	28.6 (*d*)	2α, 2β	2, 3, 4, 5, 9, 10, 14
2α	0.83 (*ddd*, *J* = 8.5, 8.5, 3.0)	9.0 (*t*)	1, 3	1, 3, 4, 10
2β	1.05–1.09 (*m*)		1, 3	1, 3, 4, 10
3	1.73–1.78 (*m*)	30.1 (*d*)	2α, 2β	1, 2, 4, 5, 10, 15
4		78.5 (*s*)		
5		164.8 (*s*)		
6		124.2 (*s*)		
7		151.1 (*s*)		
8		104.9 (*s*)		
9	3.85 (*s*)	76.7 (*d*)		1, 5, 7, 8, 10, 14
10		50.2 (*s*)		
11		122.6 (*s*)		
12		170.5 (*s*)		
13	1.62 (*s*)	10.2 (*q*)		7, 11, 12
14	0.84 (*s*)	15.4 (*q*)		1, 5, 9, 10
15α	1.69–1.72 (*m*)	41.7 (*t*)		3, 4, 5, 8′, 9′, 10′
15β	2.58–2.62 (*m*)			3, 4, 5, 8′, 9′, 10′
1′	1.65–1.69 (*m*)	25.8 (*d*)	2′α, 2′β	2′, 3′, 4′, 5′, 10′, 14′
2′α	0.62 (*ddd*, *J* = 8.5, 8.5, 4.5)	10.5 (*t*)	1′, 3′	1′, 3′, 4′, 10′
2′β	1.21–1.25 (*m*)		1′, 3′	1′, 3′, 4′, 10′
3′	1.45–1.48 (*m*)	28.6 (*d*)	2′α, 2′β	1′, 2′, 4′, 5′, 10′, 15′
4′		76.8 (*s*)		
5′	2.43 (*dd*, *J* = 12.0, 7.5)	55.4 (*d*)	6′α, 6′β	1′, 3′, 4′, 6′, 7′, 9′, 10′, 14′
6′α	2.65–2.69 (*m*)	23.7 (*t*)	5′	4′, 5′, 7′, 8′, 10′, 11′
6′β	3.10 (*dd*, *J* = 18.0, 12.0)		5′	4′, 5′, 7′, 8′, 10′, 11′
7′		174.8 (*s*)		
8′		87.0 (*s*)		
9′	2.61–2.64 (*m*)	52.1 (*d*)		4, 6, 15, 1′, 7′, 8′, 10′, 14′
10′		45.0 (*s*)		
11′		123.3 (*s*)		
12′		172.4 (*s*)		
13′a	4.53 (*d*, *J* = 12.0)	54.2 (*t*)		7′, 11′, 12′, 9″
13′b	4.90 (*d*, *J* = 12.0)			7′, 11′, 12′, 9″
14′	0.93 (*s*)	24.3 (*q*)		1′, 5′, 9′, 10′
15′a	3.79 (*d*, *J* = 11.0)	73.5 (*t*)		3′, 4′, 5′, 1″
15′b	4.78 (*d*, *J* = 11.0)			3′, 4′, 5′, 1″
1″		166.9 (*s*)		
2″	5.89 (*s*)	112.5 (*s*)		1″, 3″, 4″, 5″
3″		153.6 (*t*)		
4″	2.12 (*s*)	15.4 (*q*)		2″, 3″, 5″
5″a	4.58 (*d*, *J* = 16.0)	65.8 (*t*)		2″, 3″, 4″, 6″
5″b	5.19 (*d*, *J* = 16.0)			2″, 3″, 4″, 6″
6″		171.7 (*s*)		
7″a	2.44–2.48 (*m*)	29.2 (*t*)	8″	6″, 8″, 9″
7″b	2.65–2.69 (*m*)		8″	6″, 8″, 9″
8″a	2.81–2.84 (*m*)	29.5 (*t*)	7″	6″, 7″, 9″
8″b	2.57–2.61 (*m*)		7″	6″, 7″, 9″
9″		172.3 (*s*)		
MeO	3.45 (*s*)	51.8 (*q*)		8

[a]) Recorded in (D_6)DMSO. [b]) Recorded at 500 MHz. [c]) Recorded at 125 MHz; multiplicities inferred from DEPT and HMQC experiments. [d]) H-Atom showing long-range correlations with indicated C-atoms.

mesh) eluting with PE/AcOEt (10:0–0:10, gradient) to afford four fractions. *Fr. 2* was separated by CC (100 g SiO_2, 300–400 mesh) repeatedly, using hexane/acetone 8:1 as eluent to yield pure **2** (10.4 mg). *Fr. 3* was applied to a *Sephadex LH-20* column (8 × 150 cm, 300 g), and eluted with acetone at 15° for one day to give pure **1** (5.9 mg) and **4** (4.6 mg). *Fr. 4* was applied to a *Sephadex LH-20* column and eluted with MeOH at 15° to give pure **3** (7.9 mg) and two subfractions. *Subfr. 1* was subjected to a *Sephadex LH-20* column and eluted with MeOH. The fractions collected were purified by preparative HPLC with MeOH/H_2O 35:65 as eluent, to afford compounds **6** (8.5 mg) and **7** (9.0 mg). *Subfr. 2* was applied to preparative HPLC using MeOH/H_2O 30:70 to afford compound **5** (10.2 mg).

*5α-(Cinnamoyloxy)-8,12-epoxy-3-methoxy-7β*H*,8α*H*-eudesma-3,11-dien-6-one* (**1**). Yellowish oil. $[\alpha]_D^{24} = -36$ ($c = 0.001$, $CHCl_3$). UV (MeOH): 215 (3.27), 254 (3.15), 272 (3.10). IR: 2955, 2864, 1720, 1714, 1653, 1640, 1604, 1560, 1508, 1383, 1355, 1270, 1131, 956, 755. ^{1}H-NMR and ^{13}C-NMR: *Table 1*. ESI-MS: 431.3 ($[M+Na]^+$), 407.1 ($[M-H]^-$). HR-FT-ICR-MS: 431.1830 ($[M+Na]^+$, $C_{25}H_{28}NaO_5^+$; calc. 431.1834).

8β-(Cinnamoyloxy)eudesma-4(14),7(11)-dien-12,8-olide (**2**). Yellowish oil. $[\alpha]_D^{24} = +42$ ($c = 0.001$, $CHCl_3$). UV (MeOH): 210 (4.16), 256 (2.85), 274 (3.52). IR: 1755, 1723, 1651, 1642, 1613, 1568, 1502, 1145, 897. ^{1}H-NMR and ^{13}C-NMR: *Table 1*. ESI-MS: 401.3 ($[M+Na]^+$), 377.3 ($[M-H]^-$). HR-FT-ICR-MS: 401.1725 ($[M+Na]^+$, $C_{24}H_{26}NaO_4^+$; calc. 401.1729).

*8,12-Epoxy-1α-hydroxy-4α*H*,5α*H*-eudesma-7,11-diene-6,9-dione* (**3**). Yellowish oil. $[\alpha]_D^{24} = -22$ ($c = 0.001$, $CHCl_3$). UV (MeOH): 212 (3.46), 2.30 (3.60). IR: 3444, 2940, 2870, 1690, 1684, 1601, 1440, 1380, 1266, 1135, 1035, 937, 769. ^{1}H-NMR and ^{13}C-NMR: *Table 2*. ESI-MS: 285.2 ($[M+Na]^+$), 261.3 ($[M-H]^-$). HR-FT-ICR-MS: 285.1095 ($[M+Na]^+$, $C_{15}H_{18}NaO_4^+$; calc. 285.1103).

*8,12-Epoxy-1α-methoxy-4α*H*,5α*H*-eudesma-7,11-diene-6,9-dione* (**4**). Yellowish oil. $[\alpha]_D^{24} = -35$ ($c = 0.001$, $CHCl_3$). UV (MeOH): 210 (3.58), 2.35 (3.16). IR: 2877, 1694, 1680, 1605, 1438, 1387, 1130, 1124, 1037, 942, 761. ^{1}H-NMR and ^{13}C-NMR: *Table 2*. ESI-MS: 251.3 ($[M+H]^+$), 249.1 ($[M-H]^-$). HR-FT-ICR-MS: 251.1436 ($[M+H]^+$, $C_{16}H_{21}O_4^+$; calc. 277.1440).

Yinxiancaol (= *(1a*R*,1b*S*,1c*S*,2a*S*,2b*S*,3a*R*,3b*S*,4*R*,4a*R*,7c*R*,9a*R*,10*S*,10a*S*,14*E*)-1a,1b,1c,2,2a,2-b,3,3a,3b,4,4a,8,9,9a,10,10a-Hexadecahydro-2a,4,10-trihydroxy-4a-methoxy-1b,3b,7,15-tetramethyl-7c,8,10-(epoxypropane[1,3]diyl[2]ylideneoxybutanooxybut[2]enooxymethano)cyclopropa[4,5]cyclopropa[4′,5′]cyclopenta[1′,2′:7,8]acephenanthryleno[2,1-*b*]furan-6,13,18,21,25(1*H*)-pentone*; **5**). Amorphous white powder. M.p. 158–159°. $[\alpha]_D^{24} = -70$ ($c = 0.001$, $CHCl_3$). UV (MeOH): 225 (4.30). IR: 3448, 1766, 1730, 1373, 1282, 1130, 1122, 958, 892. ^{1}H-NMR and ^{13}C-NMR: *Table 3*. ESI-MS: 771.2 ($[M+Na]^+$). HR-FT-ICR-MS: 771.2627 ($[M+Na]^+$, $C_{40}H_{44}NaO_{14}^+$; calc. 771.2623).

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