Cyclopeptide and Terpenoids from *Tripterygium wilfordii* HOOK. F.

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The EtOH extract of dried root bark of *Tripterygium wilfordii* HOOK. F. (Celastraceae) afforded a novel macrolactone cyclopeptide named triptotin L (=cyclo[L-alanyl-L-alanyl-3-(4,4,9-trimethyldecyl-3-hydroxypropanoylglycyl-L-valyl-L-leucyl; **1**), the new triterpene 2β,6α,22β-trihydroxy-24,29-dinor-*D:A*-friedoolean-4-ene-3,21-dione named 6α-hydroxytriptocalline A (=(2β,6α,8α,9β,10α,13α,14β,20β,22β)-2,6,22-trihydroxy-9,13-dimethyl-24,25,26,30-tetranorolean-4-ene-3,21-dione; **2**), the new diterpenoid 11,16-dihydroxy-14-methoxy-18(4 → 3) *abeo*-abieta-3,8,11,13-tetraene-18-oic acid named 16-hydroxytriptobenzene H (=(4a*S*,10a*S*)-3,4,4a,9,10,10a-hexahydro-5-hydroxy-7-(2-hydroxy-1-methylethyl)-8-methoxy-1,4a-dimethylphenanthrene-2-carboxylic acid; **3**), and the abietane diterpenoid alkaloid named triptotin J (=(7a*S*,11a*S*,11b*S*)-7,7a,8,9,10,11,11a,11b-octahydro-11b-hydroxy-α,α,8,8,11a-pentamethyl-6*H*-naphth[1,2-*d*]azepine-4-methanol; **4**). Their structures were established on the basis of spectroscopic studies.

1. Introduction. – *Tripterygium wilfordii* HOOK. F. is widely distributed in China and has been used as a traditional plant insecticide and a medicinal plant. Recently anti-AIDS agents and an anti-HIV principle were isolated from this plant [1]. Many terpenoids [2] and alkaloids [3] were also isolated from this plant. For an investigation of the active principles, a careful re-examination of this species collected from the Fujian province was carried out in our laboratory. A novel macrolactone cyclopeptide and terpenoids, two of them new, were isolated from *Tripterygium wilfordii*. This paper deals with the structural investigations of these natural products.

2. Results and Discussion. – Compound **1**, obtained as a powder, had the molecular formula $C_{35}H_{63}N_5O_7$ as revealed by HR-EI-MS (*m/z* 665.4748 ($C_{35}H_{63}N_5O_7^+$; 665.4727)). This result was subsequently confirmed by observation of the fragments *m/z* 666.4561 ($[M+H]^+$) and 688.4827 ($[M+Na]^+$) in the ESI-MS of **1**. The IR spectrum showed intense NH and C=O absorptions at 3315, 1759, and 1637 cm^{-1}. The ^{13}C-NMR spectrum revealed the presence of 6 C=O (δ 170.3, 170.8, 172.1, 173.0, 173.2, and 173.5), 4 CH (δ 49.4, 50.3, 54.7, and 61.7), 1 CH_2 (δ 43.9) in the range δ 45–65, and 1 oxygenated CH groups (δ 72.9). The seven degrees of unsaturation were deduced from the molecular formula and attributed to the six C=O groups, the remaining one requiring that the molecule possesses one carbocyclic ring. These results suggested that compound **1** was a cyclopeptide [4]. The ^{1}H- and ^{13}C-NMR (*Tables 1* and *2*), ^{1}H,^{1}H-COSY, TOCSY, HMQC, HMBC, and NOESY data of **1** allowed assignment of the structure shown in *Fig. 1*. To the best of our knowledge, the macrolactone cyclopeptide **1** was isolated from this plant for the first time; we call it triptotin L.

Table 1. *^{1}H- and ^{13}C-NMR Data* (C_5D_5N) *of Amino Acid Residues of Triptotin L* (**1**). δ in ppm, J in Hz.

		^{1}H-NMR	^{13}C-NMR
Leu	NH	9.59 (d, J = 7.7, 1 H)	
	CH(α)	4.79 (m, 1 H)	54.7 (d)
	CH_2(β)	2.01 (m, 2 H)	39.7 (t)
	CH(γ)	1.97 (m, 1 H)	25.6 (d)
	Me(δ)	1.03 (d, J = 6.5, 3 H)	21.3 (q)
	Me(δ')	0.96 (d, J = 6.5, 3 H)	23.5 (q)
			172.1 (s)
Val	NH	9.19 (d, J = 6.6, 1 H)	
	CH(α)	4.76 (m, 1 H)	61.7 (d)
	CH(β)	2.47 (m, 1 H)	30.5 (d)
	Me(γ)	1.19 (d, J = 7.3, 3 H)	19.7 (q)
	Me(γ')	1.15 (d, J = 7.1, 3 H)	19.4 (q)
			173.0 (s)
Ala-1	NH	8.44 (d, J = 7.7, 1 H)	
	CH(α)	4.78 (m, 1 H)	49.4 (d)
	Me(β)	1.73 (d, J = 6.9, 1 H)	18.8 (q)
			173.5 (s)
Ala-2	NH	9.49 (d, J = 4.7, 1 H)	
	CH(α)	4.71 (m, 1 H)	50.3 (d)
	Me(β)	1.61 (d, J = 7.2, 1 H)	16.7 (q)
			173.2 (s)
Gly	NH	8.65 (d, J = 7.7, 1 H)	
	CH_2(α)	4.48 (dd, J = 17, 4.5, 1 H)	43.9 (t)
		4.84 (dd, J = 17, 4.5, 1 H)	
			170.8 (s)

Table 2. *^{1}H- and ^{13}C-NMR Data* (C_5D_5N) *of the Partial Structure $C_{16}H_{32}O_2$ of Triptotin L* (**1**[1]) δ in ppm, J in Hz.

	^{1}H-NMR	^{13}C-NMR
Me(1)	0.92 (d, J = 6.5, 3 H)	20.3 (q)
Me(2)	0.94 (d, J = 6.7, 3 H)	20.5 (q)
CH(3)	1.59 (m, 1 H)	30.3 (d)
CH_2(4)	1.32 (m, 2 H)	32.3 (t)
CH_2(5)	1.32 (m, 2 H)	27.2 (t)
CH_2(6)	1.32 (m, 2 H)	23.1 (t)
CH_2(7)	1.38 (m, 1 H), 1.11 (m, 1 H)	37.2 (t)
C(8)		30.1 (s)
CH_2(9)	1.32 (m, 1 H), 0.98 (m, 1 H)	45.3 (t)
CH_2(10)	1.54 (m, 1 H), 1.25 (m, 1 H)	32.6 (t)
CH_2(11)	1.78 (m, 1 H), 1.94 (m, 1 H)	31.7 (t)
CH(12)	5.62 (m, 1 H)	72.9 (d)
CH_2(13)	2.94 (dd, J = 14.1, 2.7, 1 H)	41.7 (t)
	2.79 (dd, J = 14.1, 7.4, 1 H)	
C(14)		170.3 (s)
Me(15,16)	0.95 (s, 6 H)	14.4 (q)

The ^{1}H-NMR spectrum of **1** clearly showed the presence of five amide protons at δ 9.59, 9.49, 9.19, 8.65, and 8.44. TOCSY Data revealed that these amide protons constituted five independent spin systems (A_3B_3MPT (NH), A_3B_3MP (NH), AX (NH), 2/A_3X (NH)), respectively. Following these five spin systems by ^{1}H,^{1}H-COSY, TOCSY, HMQC, and HMBC, the corresponding amino acid residues were determined as Leu, Val, Gly, and two Ala. The five amino acid moieties being established, the remaining structure $C_{16}H_{32}O_2$ was shown by

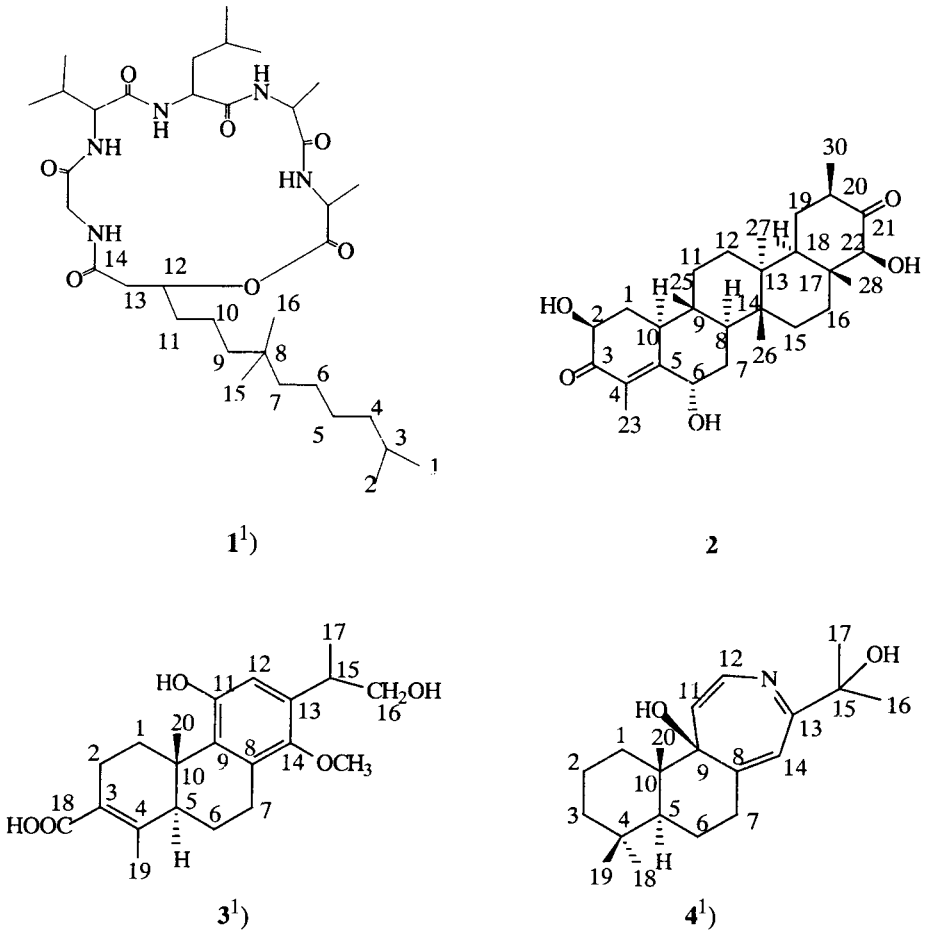

Fig. 1. *Structures of Compounds* **1**–**4**

^{1}H,^{1}H-COSY, TOCSY, and HMQC to consist of the five partial structures of *Fig. 2*. In the HMBC plot of **1**, the signal of CH_3(15,16) (δ 0.95) was correlated with the C-signals at δ 30.1 (*s*), 45.3 (*t*), 37.2 (*t*), 32.6 (*t*), and 23.1 (*t*); this clearly established that fragments **A**, **C**, and **D** were connected through the quaternary C-atom **B** (δ 30.3). Fragments **D** and **E** were connected on the basis of HMBC correlations of the C-signals at δ 30.3 (*d*) and 32.3 (*t*) to the signals of CH_3(1) (δ 0.92) and CH_3(2) (δ 0.94).

The linkages of the five amino acids were elucidated by HMBC (see *Fig. 3*). The remaining carbonyl group C(14)=O should be linked to the NH group of the glycine moiety and the O–C(12) should be part of the carboxylate group of the alanine-2 residue. The proposed structure was further confirmed by the NOESY plot, in which the amide proton at δ 9.59 (Leu) was correlated with the amide proton at δ 9.19 (Val) and 8.44 (Ala-1), the amide proton at δ 9.19 (Val) correlated with $CH_2(\alpha)$ of Gly, and the amide proton at δ 8.44 (Ala-1) correlated with the amide proton at δ 9.49 (Ala-2).

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[1]) Arbitrary numbering; for systematic names, see *Exper. Part.*

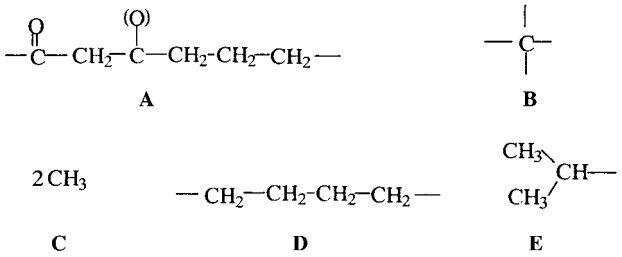

Fig. 2. *Partial structures* **A** – **E** *of* $C_{16}H_{32}O_2$

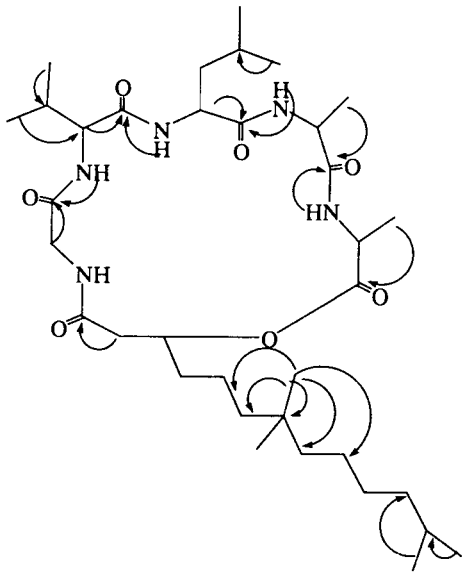

Fig. 3. *HMBC of triptotin L* (**1**)

Compound **2**, obtained as powder, showed a molecular ion $C_{28}H_{42}O_5^+$ in the high-resolution mass spectrum and two OH absorption bands at 3483 and 3456 cm^{-1}, one C=O band at 1712 cm^{-1}, and an α,β-unsaturated carbonyl band at 1674 cm^{-1} in the IR spectrum. The ^{1}H- and ^{13}C-NMR, HMQC, HMBC, and NOESY data, and their comparison with the data of triptocalline A, allowed us to establish the structure of **2** as 6α-hydroxytriptocalline A (see *Fig. 1*).

The ^{1}H-NMR spectrum of **2** revealed the presence of 6 Me (δ 0.86, 1.00, 1.08, 1.46 (4*s*), 1.20 (*d*, $J = 6.2$ Hz), and 2.15 (*d*, $J = 1.9$ Hz) and 3 CH groups (δ 4.48 (*dd*, $J = 13.8$, 6.1 Hz), 4.89 (*s*), and 5.23 (br. *s*)) attached to OH groups. The ^{13}C-NMR spectrum of **2** showed the signals of an α,β-unsaturated carbonyl moiety (δ 129.5, 157.8, and 202.3) and a six-membered-ring C=O group (δ 214.1), of six Me, seven CH_2, three oxygenated CH (δ 78.1, 72.4, and 65.4), and four CH groups and of four quaternary C-atoms. The ^{13}C-NMR data of **2** were very similar to those of triptocalline A [5], except for the chemical shifts of C(6) and C(7). The high-resolution MS revealed the presence of one more OH group in **2** compared to triptocalline A. The HMBC data of **2** confirmed that the C, D, and E rings were the same as in triptocalline A, and the ^{1}H,^{1}H-COSY and HMQC data (presence of a $CHCH_2CHOH$ moiety) suggested the same A ring for **2** and triptocalline A. The NOESY data of **2** showed a

correlation of Me(23) (δ 2.15) with H–C(6) (δ 5.23), the latter being correlated with C(6) (δ 65.4), thus establishing the position of the third OH group at C(6). The relative configuration of **2** was determined by the NOESY data (correlations of H–C(10) (δ 3.24) with H–C(2) (δ 4.48) and of H–C(22) (δ 4.89) with Me(27) (δ 1.46)). The coupling constants of H–C(2) ($J = 13.8$ and 6.1 Hz) were typical of an axial proton, and those between H–C(6) and CH_2(7) were very small. These data established the relative configuration of the OH groups of **2** as (2β,6α,22β).

Compound **3**, an amorphous powder, showed two OH absorption bands at 3230 and 3307 cm^{-1} and an α,β-unsaturated carboxylic acid band at 1676 cm^{-1} in the IR spectrum. It exhibited a molecular-ion peak at *m/z* 360.1926 (HR-EI-MS), indicating a molecular formula $C_{21}H_{28}O_5$. From the ^{1}H- and ^{13}C-NMR data, the structure of **3** was deduced to have an 18 (4 → 3) *abeo*-abietane diterpene skeleton. The further data of **3** were consistent with the structure of 16-hydroxytriptobenzene H (see *Fig. 1*).

The ^{1}H-NMR spectrum of **3** revealed the presence of 4 Me (δ 1.48 (*d*, $J = 6.9$ Hz), 1.65 (*s*), 2.47 (*d*, $J =$ 1 Hz), and 3.84 (*s*)), 1 oxygenated CH_2 (δ 4.14 (*dd*, $J = 10.5$, 6.5 Hz), 1 H and 3.98 (*dd*, $J = 10.5$, 7 Hz, 1 H) and 1 CH group (δ 7.21 (*s*)) attached to an aromatic ring. The ^{13}C-NMR spectrum of **3** showed 1 C=O signal (δ 172.1), aromatic C-atoms (δ 131.3 (*s*), 132.6 (*s*), 153.9 (*s*), 113.4 (*d*), 136.1 (*s*), and 149.7 (*s*)), 4 Me, 4 CH_2, 1 oxygenated CH_2 (δ 68.2), 2 CH, and 1 quaternary C-atom signal. These NMR data were very similar to those of triptobenzene H [6], except for the following observations. In the ^{1}H-NMR spectrum, the 2 Me signals of the ^{i}Pr group of triptobenzene H (δ 1.17 and 1.19 (*d*, $J = 6.8$ Hz)) were replaced by 1 Me signal (δ 1.48 (*d*, $J = 6.9$ Hz)) and the pattern of a CH_2 group (δ 4.14 (*dd*, $J = 10.5$, 6.5 Hz, 1 H) and 3.98 (*dd*, $J = 10.5$, 7 Hz, 1 H) in the case of **3**. The latter two protons were coupled with H–C(15) (δ 3.18) and with each other (^{1}H,^{1}H COSY); moreover, they were correlated with C(16) (δ 68.2), thus establishing the presence of an OH group at C(16). The ^{1}H,^{1}H COSY revealed the presence of a CH_2CH_2 and a $CHCH_2CH_2$ moiety in **3**, assigned to the protons at C(1) and C(2) and to those at C(5), C(6), and C(7), respectively. The remaining quaternary C-atoms were unambiguously assigned by HMBC experiment. The NOESY correlation of MeO (δ 3.84) and H–C(15) (δ 3.18) clearly indicated that the MeO group is at C(14).

Compound **4**, a yellow oil, gave a positive *Dragendorff* test. The IR spectrum of **4** showed an OH absorption band at 3411 cm^{-1}. Its molecular formula was determined by HR-EI-MS to be $C_{20}H_{31}NO_2$. The ^{1}H- and ^{13}C-NMR, HMQC, HMBC, and mass spectra and COSY experiments established the structure of **4** to be the abietane diterpenoid alkaloid triptotin J. Compound **4** is the first example of an abietane diterpenoid alkaloid isolated from the nature, which enriched the structural diversity of diterpenoids.

The ^{1}H-NMR spectrum of **4** revealed the presence of 5 Me (δ 0.79, 0.91, 1.13, 1.52, and 1.52 (each *s*), 2 definic CH (δ 7.14 (*d*, $J = 5$ Hz) and 8.41 (*d*, $J = 5$ Hz)), and 1 CH group (δ 7.34 (*s*)). The ^{13}C-NMR spectrum showed 5 Me, 5 CH_2, and 4 CH groups (δ 51.1, 117.9, 121.1, 146.1), 4 quaternary C-atoms (δ 33.3, 47.1, 156.9, and 164.8) and 2 oxygenated quaternary C-atoms (δ 71.8 and 85.6). The partial structures $CH_2CH_2CH_2$ and $CHCH_2CH_2$ were confirmed by the ^{1}H,^{1}H COSY data and assigned to the protons at C(1), C(2), and C(3) and to those at C(5), C(6), and C(7), respectively. The HMBC spectrum revealed correlations between CH_3(16,17) (δ 1.52) and C(15) (δ 71.8) and C(13) (δ 164.8), suggesting the presence of an OH group at C(15). Correlations of CH_3(20) (δ 1.13) with C(1) (δ 33.9), C(10) (δ 47.1) C(5) (δ 51.1) and C(9) (δ 85.6), and of CH_2(7) (δ 2.02, 2.29) with C(6) (δ 21.1), C(9) (δ 85.6), and C(8) (δ 156.9) were compatible with an OH group at C(9). H–C(11) (δ 7.14), which was correlated with C(11) (δ 121.2), showed a long-range correlation with C(9) (δ 85.6) and C(12) (δ 146.1). H–C(12) (δ 8.41), which was correlated with C(12) (δ 146.1), showed a long-range correlation with C(9) (δ 85.6), C(14) (δ 117.9), C(11) (δ 121.2) and C(13) (δ 164.8). The ^{1}H,^{1}H COSY established the correlation of H–C(11) (δ 7.14) and H–C(12) (δ 8.41). Thus, δ 121.2 and 146.1 were attributable to C(11) and C(12). H–C(14) (δ 7.34 (*s*)) which was correlated with C(14) (δ 117.9) showed a long-range correlation with C(9) (δ 85.6) and C(13) (δ 164.8), indicating that the signal at δ 117.9 was attributable to

C(14). The H–C(12) (δ 8.41) and C(13) (δ 164.8) signals were down-field shifted relative to the triptobenzenes A–N [7]. This fact indicated that the N-atom of **4** should be placed between C(12) and C(13). The 2D NOESY correlations of H–C(11) (δ 7.14) and H–C(14) (δ 7.34) with H_α–C(5) (δ 1.21) and H_α–C(1) (δ 0.23) revealed the relative β-configuration of OH–C(9).

Experimental Part

General. Chromatography: silica gel *60 H* from *Qingdao Haiyang Chemical Group Co.*, China. Optical rotations: *Jasco-DIP-181* polarimeter; 10-cm microcell. IR Spectra: *Perkin-Elmer-599B* IR spectrometer; KBr pellets; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker-AM-400* instrument; δ in ppm rel. to $SiMe_4$ as internal standard (= 0 ppm), *J* in Hz. MS: *MAT-711* spectrometer, in *m/z* (rel. %).

Plant Material. The roots of *Tripterygium wilfordii* were collected in Fujian Province, China. The plant material was identified by *Guan-Yuan Gu*, pharmacognosy associate professor and vice-chairman of the Scientific and Technical Archives of Shanghai Medical University, Shanghai, China. The voucher specimen is deposited in the herbarium of Shanghai Institute of Materia Medica, Chinese Academy of Sciences.

Extraction and Isolation. The air-dried roots (200 kg) of *Tripterygium wilfordii* were powdered and extracted with 95% EtOH. The EtOH extract was extracted with $CHCl_3$. The $CHCl_3$-soluble fraction (500 g) was chromatographed (silica gel, $CHCl_3$/MeOH 95 : 5, 9 : 1, 8 : 2, and 0 : 1) to give 5 fractions (*A–E*). *Fr. B* (95 g) was repeatedly chromatographed (silica gel and ODS) to give compounds **1** (5 mg), **2** (8 mg), **3** (25 mg), and **4** (27 mg).

Triptotin L (= *Cyclo[*L*-alanyl-*L*-alanyl-3-(4,4,9-trimethyldecyl)-3-hydroxypropanoyl-glycyl-*L*-valyl-*L*-leucyl]*; **1**). Amorphous powder, $[\alpha]_D^{20.0} = -33.5$ (*c* = 0.025, MeOH). IR: 3404, 3315, 2926, 1759, 1670, 1637, 1549, 1458, 1167. ^1H- and ^{13}C-NMR: *Tables 1* and *2*. EI-MS: 665 (M^+), 537, 508, 438, 294, 86, 72 (100). HR-EI-MS: 665.4748 ($C_{35}H_{63}N_5O_7^+$; 665.4727). ESI-MS: 666.4561 ($[M+H]^+$), 688.4827 ($[M+Na]^+$).

6α-Hydroxytriptocalline A (= *(2β,6α,8α,9β,10α,13α,14β,17β,18α,20β,22β)-2,6,22-trihydroxy-9,13-dimethyl-24,25,26,30-tetranorolean-4-ene-3,21-dione*; **2**). Amorphous powder. $[\alpha]_D^{20.0} = +9$ (*c* = 0.04, MeOH). IR: 3483, 3456, 1713, 1674, 1456, 1392, 1119, 989, 486. ^1H-NMR (C_5D_5N, 400 MHz): 0.86 (*s*, Me (25)); 1.00 (*s*, Me (26)); 1.08 (*s*, Me(28)); 1.46 (*s*, Me(27)); 1.20 (*d*, *J* = 6.2, Me(30)); 2.15 (*d*, *J* = 1.9, Me(23)); 3.24 (*m*, H–C(10)); 4.48 (*dd*, *J* = 13.8, 6.1, H–C(2)); 4.89 (*s*, H–C(22)); 5.23 (br. *s*, H–C(6)). ^{13}C-NMR (C_5D_5N, 400 MHz): 29.6 (*t*, C(1)); 72.4 (*d*, C(2)); 202.3 (*s*, C(3)); 129.5 (*s*, C(4)); 157.8 (*s*, C(5)); 65.4 (*d*, C(6)); 29.9 (*t*, C(7)); 40.9 (*d*, C(8)); 38.5 (*s*, C(9)); 48.9 (*d*, C(10)); 33.4 (*t*, C(11)); 29.5 (*t*, C(12)); 39.3 (*s*, C(13)); 40.6 (*s*, C(14)); 28.3 (*t*, C(15)); 29.8 (*t*, C(16)); 45.2 (*s*, C(17)); 45.8 (*d*, C(18)); 32.0 (*t*, C(19)); 41.7 (*d*, C(20)); 214.1 (*s*, C(21)); 78.1 (*d*, C(22)); 11.1 (*q*, C(23)); 17.0 (*q*, C(25)); 15.8 (*q*, C(26)); 19.3 (*q*, C(27)); 25.9 (*q*, C(28)); 15.4 (*q*, C(30)). EI-MS: 458 (45, M^+), 440 (38, $[M-H_2O]^+$), 422 (13), 289 (24), 201 (100), 156 (50), 109 (56), 95 (43). HR-EI-MS: 458.3058 ($C_{28}H_{42}O_5^+$; calc. 458.3032).

16-Hydroxytriptobenzene H (= *(4a*S*,10a*S*)-3,4,4a,9,10,10a-Hexahydro-5-hydroxy-7-(2-hydroxy-1-methylethyl)-8-methoxy-1,4a-dimethylphenanthrene-2-carboxylic Acid*; **3**). Amorphous powder. $[\alpha]_D^{20.0} = +154$ (*c* = 0.19, MeOH). IR: 3307, 3230, 1676, 1603, 1414, 1296, 1142, 1020, 860, 773. ^1H-NMR (C_5D_5N, 400 MHz): 3.90 (*m*, 1 H–C(1)); 1.94 (*m*, H–C(1)); 3.12 (*m*, 1 H–C(2)); 2.89 (*m*, 1 H–C(2)); 2.63 (br. *d*, *J* = 13, H–C(5)); 2.31 (*dd*, *J* = 12.9, 6, 1 H–C(6)); 1.72 (*m*, 1 H–C(6)); 3.36 (*dd*, *J* = 17.4, 3.8, 1 H–C(7)); 2.89 (*m*, 1 H–C(7)); 7.21 (*s*, H–C(12)); 3.18 (*m*, H–C(15)); 4.14 (*dd*, *J* = 10.5, 6.5, 1 H–C(16)); 3.98 (*dd*, *J* = 10.5, 7, 1 H–C(16)); 1.48 (*d*, *J* = 6.9, Me(17)); 2.47 (*d*, *J* = 1, Me(19)); 1.65 (3*s*, Me(20)); 3.84 (3*s*, MeO). ^{13}C-NMR (C_5D_5N, 400 MHz): 33.3 (*t*, C(1)); 26.3 (*t*, C(2)); 127.2 (*s*, C(3)); 144.7 (*s*, C(4)); 49.2 (*d*, C(5)); 20.6 (*t*, C(6)); 27.1 (*t*, C(7)); 131.3 (*s*, C(8)); 132.6 (*s*, C(9)); 38.1 (*s*, C(10)); 153.9 (*s*, C(11)); 113.4 (*d*, C(12)); 136.1 (*s*, C(13)); 149.7 (*s*, C(14)); 35.5 (*d*, C(15)); 68.2 (*t*, C(16)); 19.0 (*q*, C(17)); 172.1 (*s*, C(18)); 18.7 (*q*, C(19)); 18.5 (*q*, C(20)); 60.9 (*q*, C(21)). EI-MS: 360 (25, M^+), 345 (12), 327 (18), 290 (20), 233 (23), 201 (40), 187 (25), 149 (38), 117 (100). HR-EI-MS: 360.1926 ($C_{21}H_{28}O_5^+$; calc. 360.1937).

Triptotin J (= *(7a*S*,11a*S*,11b*S*)-7,7a,8,9,10,11,11a,11b-Octahydro-11b-hydroxy-α,α,8,8,11a-pentamethyl-6*H*-naphth[1,2-*d*]azepine-4-methanol*; **4**). Yellow oil. $[\alpha]_D^{20.0} = +21$ (*c* = 0.27, $CHCl_3$). IR: 3412, 2949, 1603, 1552, 1459, 1178, 1013, 964, 839, 733. ^1H-NMR ($CDCl_3$, 400 MHz): 0.23 (*td*, *J* = 12.9, 3.6, H_α–C(1)); 1.34 (*m*, H_β–C(1)); 1.49 (*m*, CH_2(2)); 1.32 (*m*, 1 H–C(3)); 0.66 (*td*, *J* = 14.2, 4.7, 1 H–C(3)); 1.21 (*m*, H_α–C(5)); 1.75 (*m*, CH_2(6)); 2.02 (*m*, 1 H–C(7)); 2.29 (*m*, 1 H–C(7)); 7.14 (*d*, *J* = 5, H–C(11)); 8.41 (*d*, *J* = 5, H–C(12)); 7.34 (*s*, H–C(14)); 1.52 (*s*, Me(16), Me(17)); 0.91 (*s*, Me(18)); 0.79 (*s*, Me(19)); 1.13 (*s*, Me(20)). ^{13}C-NMR ($CDCl_3$, 400 MHz): 33.9 (*t*, C(1)); 19.6 (*t*, C(2)); 40.9 (*t*, C(3)); 33.3 (*s*, C(4)); 51.1 (*d*, C(5)); 21.1 (*t*, C(6)); 37.2 (*t*, C(7)); 156.9 (*s*, C(8)); 85.6 (*s*, C(9)); 47.1 (*s*, C(10)); 121.1 (*d*, C(11)); 146.1 (*d*, C(12)); 164.8 (*s*, C(13)); 117.9

(*d*, C(14)); 71.8 (*s*, C(15)); 30.6 (*q*, C(16)); 30.7 (*q*, C(17)); 33.2 (*q*, C(18)); 20.9 (*q*, C(19)); 15.1 (*q*, C(20)). EI-MS: 317 (43, M^+), 302 (44, $[M - Me]^+$), 299 (18, $[M - H_2O]^+$), 284 (11), 193 (46), 180 (45), 164 (100), 123 (23). HR-EI-MS: 317.2362 ($C_{20}H_{31}NO_2^+$; calc. 317.2355).

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