Longistylumphyllines A – C, Three New Alkaloids from *Daphniphyllum longistylum*

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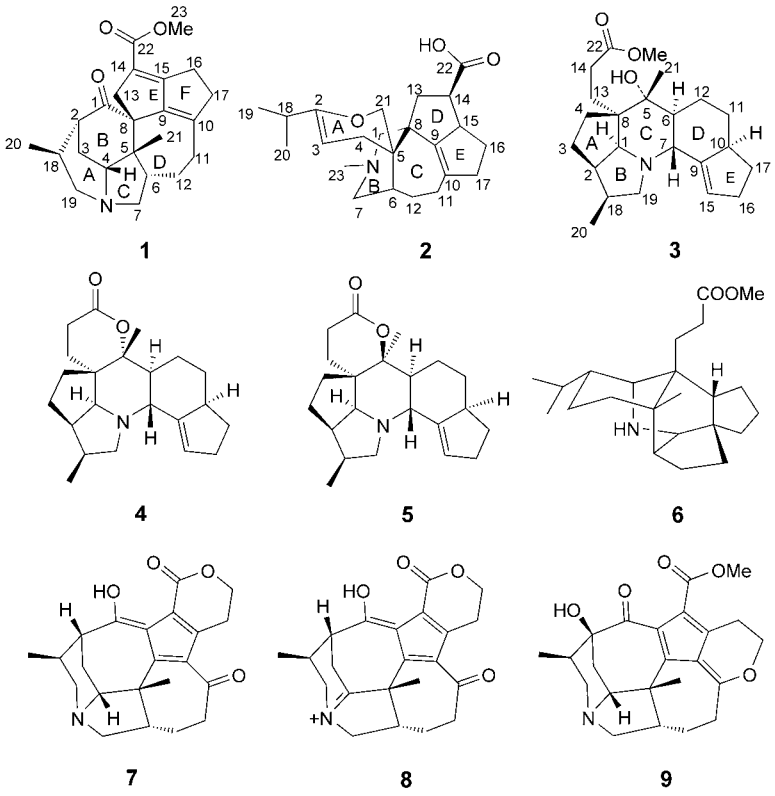
Three new alkaloids, longistylumphyllines A – C (**1** – **3**), together with the six known alkaloids deoxycalyciphylline B, deoxyisocalyciphylline B, methyl homosecodaphniphyllate, daphnicyclidin A, daphnicyclidin B, and daphnicyclidin F, were isolated from the stems and leaves of *Daphniphyllum longistylum*. Their structures and relative configuration were elucidated on the basis of spectroscopic data, especially 1D and 2D NMR techniques.

Introduction. – Plants of the genus *Daphniphyllum* contain structurally diversified alkaloids with a highly complex polycyclic skeleton [1][2]. The isolation and synthesis of *Daphniphyllum* alkaloids have attracted considerable interest. Radioactive tracer experiments revealed that the *Daphniphyllum* alkaloids are generated from six molecules of mevalonic acid *via* a squalene-like intermediate [3]. *Heathcock* and co-workers have developed an exceptionally efficient biomimetic route for the total synthesis of several polycyclic *Daphniphyllum* alkaloids [4].

Daphniphyllum alkaloids represent characteristic chemical markers for the genus *Daphniphyllum.* Recently, the chemical investigations conducted in our laboratory have led to the isolation of a number of novel alkaloids from this genus [5]. In continuation of the search for structurally interesting alkaloids, three new alkaloids, namely longistylumphyllines A (**1**), B (**2**), and C (**3**), together with the six known alkaloids **4** – **9** were isolated from the EtOH extract of the stems and leaves of *Daphniphyllum longistylum* S.S. CHIEN, which is native to the south of China [6]. This paper reports the isolation and structural elucidation of these novel alkaloids.

Results and Discussion. – Longistylumphylline A (**1**) was obtained as an optically active, colorless solid. The HR-EI-MS of **1** exhibited the molecular-ion peak at *m*/*z* 367.2149, which matched the molecular formula $C_{23}H_{29}NO_3$ with ten degrees of unsaturation. The IR absorption band at 1701 cm^{-1} implied the presence of a carbonyl group, showing up at δ 214.4 ppm in the ^{13}C-NMR. The UV absorption at 295 nm ($\log\varepsilon = 4.0$) and IR bands at 1660 and 1631 cm^{-1} indicated the presence of an ester C=O group conjugated with two C=C bonds [7]. This contention was corroborated by the ^{13}C-NMR data of the relevant C-atoms (*Table 1*) of **1** by comparison with those of the alkaloid calycicine A, which contains the same functional group [8]. Extensive analysis of the ^{1}H- and ^{13}C-NMR (*Table 1*) ^{1}H,^{1}H-COSY, HMQC, HMBC (*Table 2*),



and ROESY data allowed the assignment of structure **1** to longistylumphylline A, an alkaloid of the calyciphylline A type [9].

Two Me groups at δ 0.98 (*d*, $J = 6.1$ Hz) and 1.18 (*s*) were observed in the ^{1}H-NMR spectrum of **1**. All 23 C-atoms of the molecular formula, including 8 quaternary, 4 tertiary, and 8 secondary C-atoms, and 2 Me and 1 MeO group, appeared in the ^{13}C-NMR spectrum. Two C=O and two C=C bonds accounted for four degrees of unsaturation in **1**, and the remaining six degrees of unsaturation were assumed to indicate the presence of 6 rings. Analysis of the ^{1}H,^{1}H-COSY, HMQC, and HMBC data permitted the establishment of three structural fragments **a** (C(2) to C(4) and C(18) to C(20)), **b** (C(6) to C(7) and C(11) to C(12)), and **c** (C(16) to C(17)) drawn with bold bonds in *Fig. 1,a*. Two methylene (CH_2(19): δ(C) 49.7, δ(H) 2.83, 2.54; CH_2(7): δ(C) 54.1, δ(H) 2.86) and one methine group (CH(4): δ(C) 64.4, δ(H) 3.33) were attributable to the groups attached to the N-atom, indicating the connectivity of the partial structure **a** and **b** *via* the N-atom, which was confirmed by the HMBC correlations CH_2(19)/C(4), CH_2(19)/C(7), and CH_2(7)/C(4) (*Table 2*). In the HMBC spectrum (*Table 2*), the correlations Me(21)/C(4), C(5), and C(6), and the correlations CH_2(7)/C(5) and CH_2(12)/C(5) were observed, indicating that the partial structures **a** and **b** were also connected *via* the quaternary C(5) (δ(C) 49.5), which bears the Me(21) group. The connectivity of fragments **b** and **c** *via* C(10) and the presence of a C(9)=C(10) bond were established by the correlations CH_2(11)/C(9), C(10), and C(17), and CH_2(17)/C(10). The correlations H–C(18)/C(1) and CH_2(3)/C(1) were indicative of a linkage between C(1) and C(2); the quaternary atoms C(5) and C(8) were tentatively linked by the HMBC correlations H–C(6)/C(8) (^3J), and Me(21)/C(8) (^3J); the connectivity of C(1), C(9), and C(13) to C(8) was also tentatively made by HMBC correlations (^3J), *i.e.*, CH_2(13)/C(1), C(5), and C(9); the linkages of C(13) and C(16) to the C(14)=C(15) bond were indicated by the correlations H_a–C(13)/C(14) and C(15), and CH_2(16)/C(15), respectively. The correlations H_a–C(13)/C(9) and C(15) also implied a linkage of C(9) to C(15).

Table 1. *^1H- and ^{13}C-NMR Data of Compounds* **1**–**3**. δ in ppm, J in Hz. Trivial numbering

	1			**2**			**3**	
	δ(H)[a])	δ(C)[b])		δ(H)[c])	δ(C)[d])		δ(H)[a])	δ(C)[b])
C(1)	–	214.4	H_a–C(1)	3.11 (*d*, J = 12.2)	59.1	H–C(1)	4.49 (*t*, J = 7.2)	69.6
			H_b–C(1)	3.04 (*d*, J = 12.2)				
H–C(2)	2.19 (*d*, J = 1.9)	43.7	C(2)	–	161.2	H–C(2)	2.64 (*m*)	51.8
CH_2(3)	2.02 (*m*)	20.1	H–C(3)	4.46 (*dd*, J = 5.0, 1.5)	91.7	H_a–C(3)	1.67 (*m*)	26.9
						H_b–C(3)	1.58 (*m*)	
H–C(4)	3.33 (*d*, J = 4.0)	64.4	H_a–C(4)	2.29 (*d*, J = 16.9)	28.8	H_a–C(4)	1.43 (*m*)	34.7
			H_b–C(4)	2.02 (*d*, J = 16.9		H_b–C(4)	2.13 (*m*)	
C(5)	–	49.5	C(5)	–	41.0	C(5)	–	73.5
H–C(6)	2.28 (*m*)	51.7	H–C(6)	2.26 (*m*)	37.6	H–C(6)	1.66 (*m*)	49.7
CH_2(7)	2.86 (*m*)	54.1	H_a–C(7)	3.35 (*dd*, J = 14.2, 5.9)	56.1	H–C(7)	4.34 (br. *s*)	58.6
			H_b–C(7)	3.45 (*d*, J = 13.6)				
C(8)	–	60.8	C(8)	–	47.2	C(8)	–	50.5
C(9)	–	149.0	C(9)	–	144.7	C(9)	–	139.8
C(10)	–	152.4	C(10)	–	137.9	H–C(10)	2.95 (br. *s*)	41.1
H_a–C(11)	2.01 (*m*)	25.4	H_a–C(11)	2.35 (*m*)	27.0	H_a–C(11)	2.11 (*m*)	34.4
H_b–C(11)	2.13 (*m*)		H_b–C(11)	2.41 (*m*)		H_b–C(11)	0.87 (*dd*, J = 22.9, 11.5)	
CH_2(12)	1.81 (*m*)	24.4	H_a–C(12)	2.32 (*m*)	26.9	H_a–C(12)	1.65 (*m*)	25.5
			H_b–C(12)	1.67 (*m*)		H_b–C(12)	1.80 (*m*)	
H_a–C(13)	2.87 (*m*)	45.6	H_a–C(13)	1.78 (*dd*, J = 14.9, 9.1)	41.0	H_a–C(13)	1.92 (*m*)	32.7
H_b–C(13)	3.49 (br. *d*, J = 16.8)		H_b–C(13)	2.56 (*dd*, J = 14.9, 2.6)		H_b–C(13)	1.65 (*m*)	
C(14)	–	114.5	H–C(14)	2.84 (*m*)	45.1	H_a–C(14)	2.62 (*m*)	29.1
						H_b–C(14)	2.23 (*m*)	
C(15)	–	170.9	H–C(15)	3.57 (*m*)	56.2	H–C(15)	5.81 (*s*)	132.8
CH_2(16)	2.71 (*m*)	25.4	H_a–C(16)	1.93 (*m*)	29.5	H_a–C(16)	2.38 (*m*)	31.4
			H_b–C(16)	1.60 (*m*)		H_b–C(16)	2.32 (*m*)	
H_a–C(17)	3.00 (br. *d*, J = 18.2)	42.3	H_a–C(17)	2.70 (*m*)	44.2	H_a–C(17)	2.17 (*m*)	30.6
H_b–C(17)	2.90 (br. *d*, J = 18.2)		H_b–C(17)	2.42 (*m*)		H_b–C(17)	1.34 (*m*)	
H–C(18)	2.78 (*m*)	33.0	H–C(18)	2.22 (*m*)	33.7	H–C(18)	2.53 (*m*)	32.7
H_a–C(19)	2.83 (*m*)	49.7	Me(19)	1.02 (*d*, J = 6.9)	21.0	H_a–C(19)	3.81 (*m*)	60.7
H_b–C(19)	2.54 (*dd*, J = 13.7, 9.3)					H_b–C(19)	2.77 (*dd*, J = 20.9, 10.3)	
Me(20)	0.98 (*d*, J = 6.1)	19.0	Me(20)	1.02 (*d*, J = 6.9)	21.1	Me(20)	0.98 (*d*, J = 6.7)	11.9
Me(21)	1.18 (*s*)	23.2	H_a–C(21)	4.42 (*dd*, J = 11.9, 2.6)	70.6	Me(21)	1.39 (*s*)	25.3
			H_b–C(21)	4.06 (br. *d*, J = 11.9)				
C(22)	–	166.4	C(22)	–	179.7	C(22)	–	173.7
MeO	3.68 (*s*)	51.0	MeN	2.84 (*s*)	46.3	MeO	3.67 (*s*)	51.8

[a]) Measured at 600 MHz in $CDCl_3$. [b]) Measured at 100 MHz in $CDCl_3$. [c]) Measured at 600 MHz in CD_3OD. [d]) Measured at 100 MHz in CD_3OD.

Table 2. *HMBC Correlations of Compounds* **1**–**3**. Trivial numbering.

1 (H→C)[a])		**2** (H→C)[b])		**3** (H→C)[a])	
		H_a–C(1)	C(5), C(7), C(8), C(9)	H–C(1)	C(3), C(4), C(5),
		H_b–C(1)	C(5), C(8), C(9), C(23)		C(18), C(19)
H–C(2)	C(3), C(4)			H–C(2)	C(3), C(4),
					C(18), C(19)
CH_2(3)	C(1), C(2), C(4),	H–C(3)	C(2), C(4), C(5), C(18)	H_a–C(3)	C(1), C(8)
	C(5), C(6), C(18)			H_b–C(3)	C(1), C(8)
H–C(4)	C(2)	H_a–C(4)	C(2), C(3), C(6), C(21)	H_a–C(4)	C(1), C(5), C(8)
		H_b–C(4)	C(2), C(3), C(5),	H_b–C(4)	C(1), C(2),
			C(6), C(8)		C(3), C(5), C(8)
H–C(6)	C(5), C(7), C(8), C(11),	H–C(6)	C(4), C(5), C(7), C(8),	H–C(6)	C(8)
	C(12), C(21)		C(12), C(21)		
CH_2(7)	C(4), C(5), C(6), C(19)	H_a–C(7)	C(1), C(5), C(6), C(12)	H–C(7)	C(9), C(10),
		H_b–C(7)	C(6), C(12), C(23)		C(15), C(19)
				H–C(10)	C(11)
H_a–C(11)	C(9), C(10), C(17)	H_a–C(11)	C(6), C(9), C(10), C(12)	H_a–C(11)	C(9)
H_b–C(11)	C(10), C(12)	H_b–C(11)	C(9), C(10), C(12)	H_b–C(11)	–
CH_2(12)	C(5), C(6), C(7), C(10)	H_a–C(12)	C(5), C(6), C(7),	H_a–C(12)	C(6), C(10)
			C(10), C(11)		
		H_b–C(12)	C(5), C(6), C(7),	H_b–C(12)	C(5)
			C(10), C(11)		
H_a–(13)	C(1), C(5), C(9),	H_a–C(13)	C(1), C(5), C(8),	H_a–C(13)	C(4), C(8)
	C(14), C(15)		C(14), C(22)		
H_b–(13)	C(14)	H_b–C(13)	C(1), C(8), C(9),	H_b–C(13)	C(1), C(5), C(8)
			C(14), C(22)		
		H–C(14)	C(8), C(22)	H_a–C(14)	C(13), C(22)
				H_b–C(14)	C(8)
		H–C(15)	–	H–C(15)	C(7), C(9), C(10),
					C(16), C(17)
CH_2(16)	C(15), C(17)	H_a–C(16)	C(9), C(10), C(15)	H_a–C(16)	C(9), C(15)
		H_b–C(16)	–	H_b–C(16)	C(9), C(15)
H_a–(17)	C(9), C(10), C(16)	H_a–C(17)	–	H_a–C(17)	C(9), C(15)
H_b–(17)	C(9), C(10)	H_b–C(17)	C(9), C(10), C(15),	H_b–C(17)	C(10), C(11)
			C(16)		
H–C(18)	C(1), C(2), C(3),	H–C(18)	C(2), C(3), C(19),	H–C(18)	C(2), C(3),
	C(19), C(20)		C(20)		C(19), C(20)
H_a–C(19)	C(2), C(4), C(7),	Me(19)	C(2), C(18), C(20)	H_a–C(19)	C(1), C(2)
	C(18), C(20)				
H_b–C(19)	C(2), C(4), C(7),			H_b–C(19)	–
	C(18), C(20)				
Me(20)	C(2), C(18), C(19)	Me(20)	C(2), C(18), C(19)	Me(20)	C(2), C(18), C(19)
Me(21)	C(4), C(8), C(6),	H_a–C(21)	C(2), C(4)	Me(21)	C(5), C(6), C(8)
	C(5), C(13)	H_b–C(21)	C(4), C(6)		
MeO	C(22)	MeN	C(1), C(6), C(7)	MeO	C(22)

[a]) Measured at 400 MHz in $CDCl_3$. [b]) Measured at 400 MHz in CD_3OD.

The relative configuration of **1** could be determined by a ROESY experiment (*Fig. 1,b*). The ROESY correlation Me(21)/H_b–C(13) indicated that C(13) and C(21) were on the same side, and were assumed to be in β-orientation as those of calyciphylline A; the correlations Me(21)/H–C(4), Me(21)/H–C(6), and Me(20)/H–C(2), Me(20)/H_b–C(19), and H–C(2)/H_a–C(13) indicated that H–C(2), H–C(4), H–C(6), H_b–C(19), Me(20), and Me(21) were all on the same side. The ROESY correlations H–C(3)/H_b–C(19) and H–C(3)/H_a–C(13) suggested that the A- and B-rings are presented in a boat conformation. The correlation Me(21)/H–C(12) inferred that the seven-membered D-ring assumes a chair-like conformation.

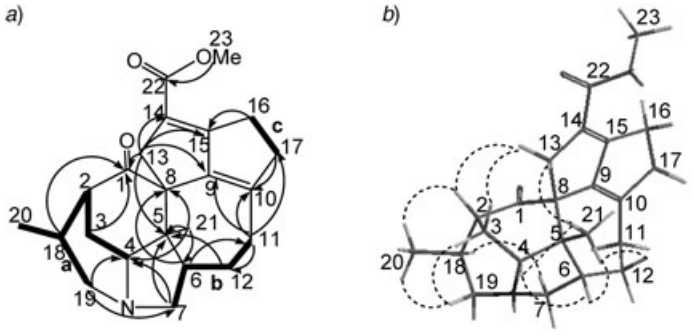


Fig. 1. a) *$^1H,^1H$-COSY* (▬) *and key HMBC correlations* (H⌒C) *of* **1**; b) *key ROESY correlations* (H⋯H) *of* **1**

The molecular formula of longistylumphylline B (**2**) was determined as $C_{23}H_{33}NO_3$ by HR-EI-MS (see *Exper. Part*). The IR absorption bands at 3427 and 1647 cm^{-1} indicated the presence of OH and C=O functionalities, respectively. The ^1H- and ^{13}C-NMR (*Table 1*) and 2D-NMR data (*Table 2* and *Fig. 2*) established structure **2** for longistylumphylline B.

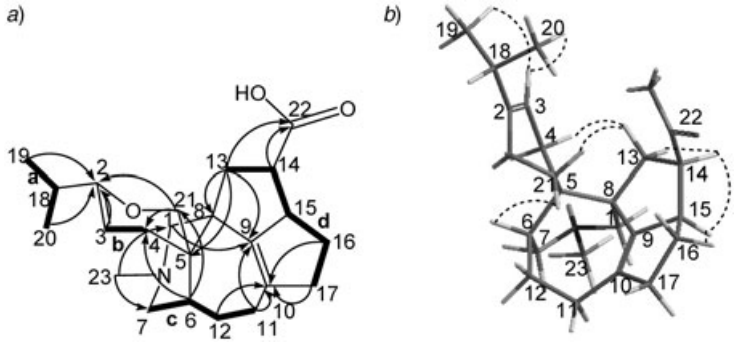


Fig. 2. a) *$^1H,^1H$-COSY* (▬) *and key HMBC correlations* (H⌒C) *of* **2**; b) *key ROESY correlations* (H⋯H) *of* **2**

The ^{13}C-NMR spectrum of **2** showed 23 signals due to 6 quaternary C-atoms, 5 CH, 9 CH_2, and 3 Me groups. Among them, two sp^3 CH_2 units (δ(C) 59.1, δ(H) 3.11 and 3.04; δ(C) 56.1, δ(H) 3.45 and 3.35) and one Me group (δ(C) 46.3, δ(H) 2.84) were ascribable to be connected with the N-atom. Two C=C bonds and one C=O group accounted for three out of eight degrees of unsaturation, suggesting that compound **2** contains 5 rings. The spectral data of **2** is similar to the reported values of a dehydration product of daphnigracine [10], except for the absence of the MeO group at C(22). The constitution of **2** was determined by interpretation of the $^1H,^1H$-COSY, HMQC, and HMBC data (see *Fig. 2,a* and *Table 2*). The relative configuration of **2** was deduced from the ROESY data (*Fig. 2,b*), in which the observed interactions $H_b-C(4)/H_b-C(13)$ and $H_b-C(21)/H_b-C(13)$ indicated that $H_b-C(4)$, $H_b-C(13)$, and $H_b-C(21)$ were on the same side and assumed as β-oriented. $H_a-C(13)$, H−C(14), H−C(15), $H_a-C(16)$, and $H_a-C(17)$ were assigned to be on the α-side as judged from the correlations $H_a-C(13)/H-C(14)$, $H-C(14)/H-C(15)$, $H-C(15)/H_a-C(16)$, and $H_a-C(16)/H_a-C(17)$. The correlation $H-C(6)/H_a-C(21)$ indicated a β-orientation for H−C(6).

Longistylumphylline C (**3**) has the molecular formula $C_{23}H_{35}NO_3$ as determined by HR-EI-MS data (*m/z* 373.2599). IR Absorption bands at 3500 and 1740 cm^{-1} indicated

the presence of an OH group and an ester C=O unit. The ^{1}H-NMR and ^{13}C-NMR data of **3** and **4** (*Table 1*) showed a high similarity, implying that they are structurally closely related. Compared to **4**, alkaloid **3** shows a MeO signal (δ(H) 3.67), suggesting that the six-membered lactone of **4** is opened in **3** and the resulting carboxyl group esterified. The location of the MeO group at C(22) was determined by the HMBC correlation MeO/C(22) (δ(C) 173.7). The structure of **3** was confirmed by the interpretation of the ^{1}H,^{1}H-COSY, HMQC, and HMBC data (*Fig. 3*,*a* and *Table 2*). The relative configuration of **3** is identical to that of **4** (ROESY evidence, *Fig. 3*,*b*).

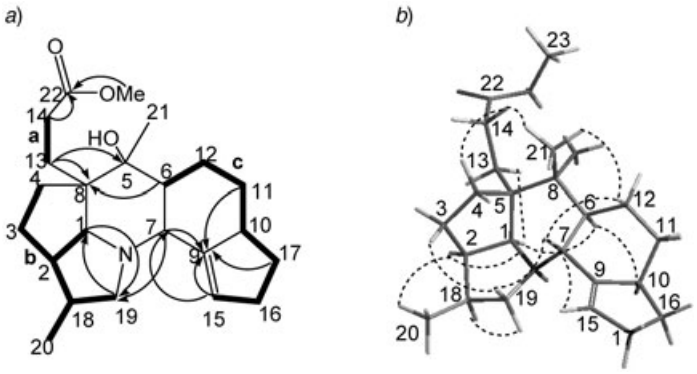


Fig. 3. a) *^{1}H,^{1}H-COSY* (—) *and key HMBC correlations* (H⌒C) *of* **3**; b) *key ROESY correlations* (H⋯H) *of* **3**

The known alkaloids deoxycalyciphylline B (**4**) and deoxyisocalyciphylline B (**5**) were identified by their spectral data (EI-MS, ^{1}H- and ^{13}C-NMR) and direct comparison with authentic samples (co-TLC) [5]. The known alkaloids homosecodaphniphyllate (**6**), daphnicyclidin A (**7**), daphnicyclidin B (**8**), and daphnicyclidin F (**9**) were identified on the basis of their reported spectral data (EI-MS, ^{1}H- and ^{13}C-NMR) [11][2].

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Experimental Part

General. All solvents used were of anal. grade (*Shanghai Chemical Plant*, Shanghai, P.R. China). Column chromatography (CC): silica gel (230–400 mesh), C_{18} reverse-phased silica gel (150–200 mesh, *Merck*), or amino silica gel (20–45 μm). TLC: precoated silica gel GF_{254} plates (*Qingdao Marine Chemical Plant,* Qingdao, P.R. China).

Optical rotations: *Perkin-Elmer 341* polarimeter. IR Spectra: *Perkin-Elmer 577* spectrometer; KBr discs. NMR Spectra: *Bruker AM-400* and *Bruker AM-600* spectrometers; $SiMe_4$ as internal standard. EI-MS (70 eV): *Finnigan MAT-95* mass spectrometer in *m*/*z* (rel. %).

Plant Material. Daphniphyllum longistylum was collected from Guangdong province of P.R. China and authenticated by Prof. *Suhua Shi* of the Institute of Botany, School of Life Science, Zhongshan University, P.R. China. A voucher specimen was deposited in the Herbarium of the Institute of Materia Medica, Shanghai Institutes for Biological Sciences, Chinese Academy of Sciences (accession number DL-2002-1Y).

Extraction and Isolation. The dry leaves and stems (4.0 kg) of *D. longistylum* were ground and percolated with 95% EtOH. After evaporation of the EtOH, the crude extract was dissolved in 1 l of H_2O to form a

suspension and then acidified with 0.25M H_2SO_4 to pH *ca.* 5. The acidic suspension was immediately extracted with AcOEt (6 × 300 ml) to remove the nonalkaloid components. The acidic aq. phase was adjusted with 1M Na_2CO_3 to pH *ca.* 10 and extracted with $CHCl_3$ (6 × 300 ml) to give the crude alkaloids (2.0 g). This mixture was subjected to CC (silica gel, $CHCl_3$/MeOH 10:1): *Fractions 1–5*. *Fr. 1* (300 mg) was purified by CC (amino silica gel, cyclohexane/AcOEt 10:1): **4** (22.5 mg, 0.0006%) and **5** (18.0 mg, 0.0005%). *Fr. 2* (80 mg) was subjected to CC (amino silica gel, cyclohexane/AcOEt 6 :1): **6** (5.0 mg, 0.0001%). *Fr. 3* was separated by CC (amino silica gel, $CHCl_3$): **3** (10.0 mg, 0.0002%) followed by **1** (5.0 mg, 0.0001%). *Fr. 4* was purified by CC (C_{18} reversed-phase silica gel, MeOH/H_2O/HCOOH 5:5:0.001): **7** (7 mg, 0.0002%), **8** (10 mg, 0.0003%), and **9** (6 mg, 0.0002%). *Fr. 5* was purified by CC (silica gel, $CHCl_3$/MeOH/H_2O 2:1:0.1): **2** (18 mg, 0.0005%).

Longistylumphylline A (*= (6aS*,10S*,11R*,12aR*,12bS*,12cR*)-3,4,5,6,6a,7,9,10,11,12,12a,12b-Dodecahydro-10,12b-dimethyl-13-oxo-1*H*-11,12c-methanocyclopent[1,8]azuleno[4,5*-b*]indolizine-2-carboxylic Acid Methyl Ester;* **1**). Colorless oil. $[\alpha]_D^{20} = -78$ ($c = 0.8$, $CHCl_3$). UV (MeOH): 295 (log $\varepsilon = 4.0$). IR (KBr): 2925, 1701, 1660, 1632, 1439, 1385, 1126, 1064. ^{1}H- and ^{13}C-NMR: *Table 1*. EI-MS (70 eV): 367 (36, M^+), 336 (4), 308 (4), 242(9), 139(15). HR-EI-MS: 367.2149 (M^+, $C_{23}H_{29}NO_3^+$; calc. 367.2147).

Longistylumphylline B (*= (4S*,9R*,10aR*,11S*)-2,3,4,5,6,7,8,8a,9,10-Decahydro-2-methyl-6′-(1-methylethyl)spiro[1*H*-4,10a-methanopentaleno[1,6-*ed*]azonine-11,3′(4′*H*)-[2*H*]pyran]-9-carboxylic Acid;* **2**). White powder. $[\alpha]_D^{20} = -10$ ($c = 0.5$, MeOH/$CHCl_3$ 7:3). IR (KBr): 3427, 2960, 1704, 1673, 1467, 1454, 1380, 1292, 1195, 1087. ^{1}H- and ^{13}C-NMR: *Table 1*. EI-MS (70 eV): 371 (29, M^+), 328 (7), 300 (31), 286(15), 273(19), 228(9). HR-EI-MS: 371.2458 (M^+, $C_{23}H_{33}NO_3^+$; calc. 371.2460).

Longistylumphylline C (*= (2S*,2aR*,4aS*,5R*,5aS*,7aR*,10bR*,11aS*)-1,2,2a,3,4,5,5a,6,7,7a,8,9,10b,11a-Tetradecahydro-5-hydroxy-2,5-dimethyl-4a*H*-cyclopent[*hi*]indeno[4,5-*e*]indolizine-4a-propanoic Acid Methyl Ester;* **3**). Colorless oil. $[\alpha]_D^{20} = 19$ ($c = 1.0$, $CHCl_3$). IR (KBr): 3500, 2954, 2870, 1740, 1463, 1377, 1286, 1170, 1122, 1072. ^{1}H- and ^{13}C-NMR: *Table 1*. EI-MS (70 eV): 373 (100, M^+), 355 (59), 345 (53), 340(35), 300(24), 268(44), 254(27). HR-EI-MS: 373.2599 (M^+, $C_{23}H_{35}NO_3^+$; calc. 373.2617).

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