Yunnandaphninines F and G, New C_{30} Alkaloids from *Daphniphyllum yunnanense*

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Eight C_{30} *Daphniphyllum* alkaloids, including two new ones, yunnandaphninines F and G (**1** and **2**, resp.), were isolated from the leaves and stems of *Daphniphyllum yunnanense*. Their structures were elucidated on the basis of the spectroscopic data.

Introduction. – *Daphniphyllum* alkaloids are a family of structurally diversified alkaloids with polycyclic ring systems elaborated by trees of the genus *Daphniphyllum* [1–5]. These compounds have attracted great interest as challenging targets for total synthesis and biosynthetic research [1].

In our search for structurally unique and biogenetically interesting *Daphniphyllum* alkaloids, we reported more than 30 new fused-heterocyclic ones from various species, some of which possess unprecedented ring systems [2]. As further investigation on the leaves and stems of *D. yunnanense*, two new C_{30} alkaloids, yunnandaphninines F and G (**1** and **2**, resp.), were obtained, together with six known C_{30} alkaloids: yunnandaphninine H (**3**) [6], daphnilongeridine (**4**) [7], daphmacropodine (**5**) [8], daphmacrine (**6**) [9], daphnilongeranin D (**7**) [10], and codaphniphylline (**8**) [6]. Here, we describe the isolation and structural elucidation of the new compounds **1** and **2**.

Result and Discussion. – ESI-MS Data of yunnandaphninine F (**1**) showed the pseudomolecular ion at m/z 486 ($[M+H]^+$), and the molecular formula $C_{30}H_{47}NO_4$ was established by HR-ESI-MS (m/z 486.3580). The IR spectrum implied the presence of OH (3459 cm^{-1}) and C=O (1748 cm^{-1}) functions. The ^{13}C-NMR (*Table 1*) data of **1** displayed 30 signals, including one lactone CO-group, five sp^3 quaternary C-atoms, eight sp^3 CH groups, eleven sp^3 CH_2 groups, and five Me groups. Among them, one CH group (δ(C) 64.8) and one quaternary C-atom (δ(C) 71.9) were ascribed to those bearing an N-atom, one CH group (δ(C) 68.2) and one quaternary C-atom (δ(C) 86.3) were attributed to those bearing an O-atom, and one CH group (δ(C) 80.2) bore an O- and an N-atom.

The ^{1}H,^{1}H-COSY, HMQC, and TOCSY of **1** revealed connectivities of five partial structures (*Fig. 1*, *a*[1])): *A* (C(1) to C(4), C(2) to C(18), and C(18) to C(19) and C(20)),

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

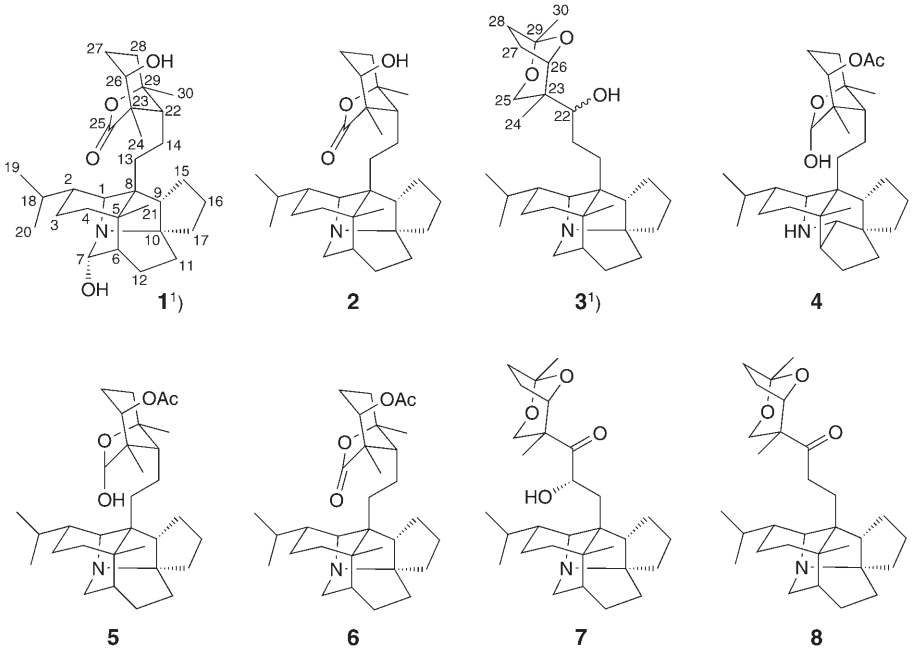

Table 1. *^{13}C-NMR Data of* **1**, **2**, *and* **3**[1]). At 400 MHz, in $CDCl_3$; δ in ppm.

	1	**2**	**3**		**1**	**2**	**3**
C(1)	64.8 (*d*)	64.0 (*d*)	62.9 (*d*)	C(16)	24.7 (*t*)	25.3 (*t*)	25.5 (*t*)
C(2)	37.8 (*d*)	38.1 (*d*)	38.0 (*d*)	C(17)	41.4 (*t*)	39.1 (*t*)	41.8 (*t*)
C(3)	26.8 (*t*)	25.7 (*t*)[a])	22.7 (*t*)	C(18)	30.7 (*d*)	29.7 (*d*)	31.0 (*d*)
C(4)	36.0 (*t*)	35.9 (*t*)	36.9 (*t*)	C(19)	21.2 (*q*)	21.7 (*q*)	21.6 (*q*)
C(5)	37.9 (*s*)	37.1 (*s*)	37.2 (*s*)	C(20)	20.6 (*q*)	20.7 (*q*)	21.1 (*q*)
C(6)	46.9 (*d*)	38.8 (*d*)	38.0 (*d*)	C(21)	25.7 (*q*)	25.3 (*q*)	24.0 (*q*)
C(7)	80.2 (*d*)	45.9 (*t*)	47.2 (*t*)	C(22)	56.7 (*d*)	56.4 (*d*)	74.8 (*d*)
C(8)	47.9 (*s*)	47.6 (*s*)	48.1 (*s*)	C(23)	50.9 (*s*)	50.7 (*s*)	40.0 (*s*)
C(9)	50.8 (*d*)	50.7 (*d*)	51.6 (*d*)	C(24)	18.1 (*q*)	18.7 (*q*)	15.5 (*q*)
C(10)	71.9 (*s*)	77.9 (*s*)	77.2 (*s*)	C(25)	180.2 (*s*)	178.6 (*s*)	67.0 (*t*)
C(11)	29.2 (*t*)	27.6 (*t*)	26.0 (*t*)	C(26)	68.2 (*d*)	69.0 (*d*)	81.8 (*d*)
C(12)	17.1 (*t*)	21.1 (*t*)	27.1 (*t*)	C(27)	25.5 (*t*)	25.7 (*t*)[a])	24.8 (*t*)
C(13)	31.3 (*t*)	31.4 (*t*)	28.5 (*t*)	C(28)	28.1 (*t*)	28.6 (*t*)	33.8 (*t*)
C(14)	24.4 (*t*)	24.2 (*t*)	29.3 (*t*)	C(29)	86.3 (*s*)	85.4 (*s*)	104.9 (*s*)
C(15)	28.6 (*t*)	29.3 (*t*)	29.7 (*t*)	C(30)	23.8 (*q*)	24.0 (*q*)	24.5 (*q*)

[a]) Overlapped.

B (C(6) to C(7) and C(12), and C(11) to C(12)), *C* (C(13) to C(14), and C(14) to C(22)), *D* (C(9) to C(15), and C(15) to C(17)), and *E* (C(26) to C(28)). HMBC correlations from H–C(7) to C(1) and C(10) indicated that C(1), C(7), and C(10) were connected to each other through an N-atom. Connections between C(4), C(6), and C(21) *via* C(5) were suggested by HMBC cross-peaks of CH_2(4), H–C(6), and Me(21)

to C(5). On the other hand, connections among C(11) and C(17) *via* C(10) were indicated by HMBC cross-peaks of H–C(11) and H–C(17) to C(10). HMBC cross-peaks of H–C(1) to C(5) and C(8), CH_2(13) to C(1), C(8), and C(9), and Me(21) to C(8) suggested connectivities among units *A* – *D*, forming an N-containing hexacyclic skeleton like daphnimacropine [11]. Furthermore, the presence of a 2-hydroxy-1,5-dimethyl-6-oxabicyclo[3.2.1]octan-7-one moiety including unit *E* was deduced from HMBC cross-peaks of Me(24) to C(22), C(23), C(25), and C(26), Me(30) to C(22), C(28), and C(29). Thus, gross structure of **1** was elucidated as shown.

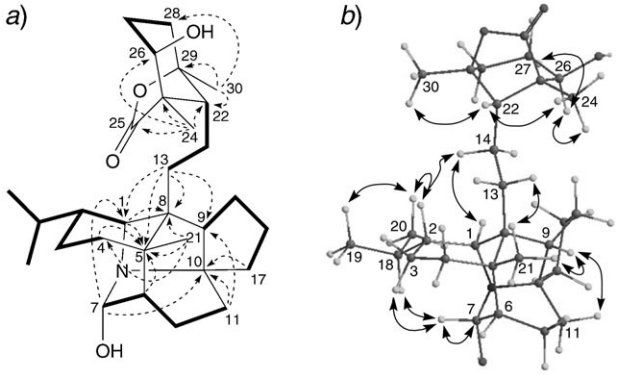

Fig. 1. a) *Key* $^1H,^1H$*-COSY and TOCSY* (—)*, and HMBC correlations* (- - →) *for* **1**[1]). b) *Key ROESY correlations* (↔) *for* **1**[1]).

The correlations of H–C(7)/H_a–C(3) and H–C(7)/H–C(18) in its ROESY spectrum indicated that H–C(7) had β-orientation (*Fig. 1*, *b*). In addition, the relative configuration at the remaining stereogenic centers of **1** should be as shown on the basis of the ^{13}C-NMR shifts and NOE data.

ESI-MS Data of yunnandaphninine G (**2**) showed the pseudomolecular ion at *m*/*z* 470 ($[M+H]^+$), and the molecular formula $C_{30}H_{47}NO_3$ was established by HR-ESI-MS (*m*/*z* 470.3627). The IR absorption implied the presence of OH (3419 cm^{-1}) and C=O (1764 cm^{-1}) functions. The ^{13}C-NMR (*Table 1*) spectra of **2** gave signals including one lactone CO group, five sp^3 quaternary C-atoms, seven sp^3 CH groups, twelve sp^3 CH_2 groups, and five Me groups. Among them, one CH group (δ(C) 64.0), one CH_2 group (δ(C) 45.9), and one quaternary C-atom (δ(C) 77.9) were ascribed to those bearing an N-atom, while one CH group (δ(C) 69.0) and one quaternary C-atom (δ(C) 85.4) were attributed to those bearing an O-atom. Comparison of NMR data of **2** with those of daphmacropodine **5** revealed that the structure of **2** resembled that of the latter [8]. Furthermore, the upfield shift of *ca.* 5 ppm for the oxygenated CH group, and lack of an Ac group implied that structure of **2** should be 26-deacetyl daphmacropodine, which was confirmed by 2D-NMR experiments as shown in *Fig. 2*[1]). Furthermore, the relative configuration of **2** was deduced to be same as that of **1** on the basis of ^{13}C-NMR shifts and NOE data.

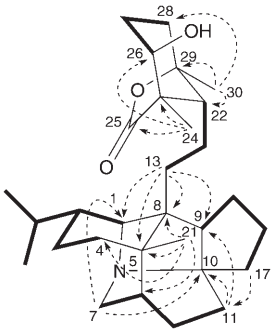

Fig. 2. *Key* $^1H,^1H$*-COSY and TOCSY* (—)*, and HMBC correlations* (- - →) *for* **2**[1])

Yunnandaphninine H (**3**) has been first reported as synthetic intermediate of codaphniphylline by *Heathcock et al.* [7]. However, no spectral data were published. In this paper, we present the full ^1H- and ^{13}C-NMR data for **3** (*Tables 2* and *1*).

The cytotoxic activities of all compounds (**1**–**8**) against the growth of tumor cell lines (P-388 (mouse lymphocytic leukemia), and A549 (human lung adenocarcinoma)) were evaluated. The results indicated that all alkaloids were inactive against the above cancer cell lines (50% effective dose of clonal inhibition (ED_{50}) > 10 μg/ml).

Experimental Part

General. TLC: On silica-gel plates; visualization by *Dragendorff* reagent. Column chromatography (CC): Silica gel *H* (10–40 μm; *Qingdao Marine Chemical Ltd. Co.*), amino silica gel (90–140 μm, *Fuji Silysia Chemical Ltd.*), *Sephadex LH-20* (40–70 μm, *Pharmacia*), and *Lichroprep RP-18* gel (40–63 μm, *Merck*). The MPLC instrument includes a *Büchi Pump Module C-605*, and a *Büchi Pump Manager C-615*. Optical rotations: *JASCO DIP-370* digital polarimeter. IR Spectra: *Bio-Rad FTS-135* spectrometer, KBr pellets, in cm^{-1}. NMR spectra: *Bruker AM-400* instrument (400/100 MHz) and *Bruker DRX-500* instrument (500/125 MHz); δ in ppm rel. to TMS as internal standard, *J* in Hz. ESI-MS: *Finnigan MAT 90* instrument; in *m*/*z*. HR-ESI-MS: and *API Qstar Pulsar LC*/*TOF* instrument.

Plant Material. The leaves and twigs of *Daphniphyllum yunnanense* were collected in Xishuangbanna of Yunnan Province, P. R. China, in April 2005. The material was identified by Prof. *Shun-Cheng Zhang*, Xishuangbanna Tropical Botanical Garden, Chinese Academy of Sciences, and a specimen (KIB 05050217) was deposited at the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation. Air-dried and powdered leaves and twigs of *D. yunnanense* (7.0 kg) were extracted with 95% EtOH, and the extract was partitioned between AcOEt and 0.001N HCl. The aq. layer was then alkalinized to pH 10 with 2N NaOH followed by exhaustive extraction with $CHCl_3$. $CHCl_3$-soluble materials were roughly separated by CC (amino silica gel (450g, 90–140 μm); $CHCl_3$/MeOH 1:0 to 0:1) to afford *Fr. A*–*E*. *Fr. B* was separated by CC (*RP-18*; MeOH/ 0.1% TFA, 1:9 to 8:2) to afford *Fr. 1*–*8*, of which *Fr. 5* was subjected by CC (*Sephadex LH-20*; $CHCl_3$/MeOH 1:1; and silica gel; $CHCl_3$/MeOH 50:1 to 10:1) to give **6** (15 mg), **7** (9 mg), and **8** (8 mg). Similarly, *Fr. C* was separated by CC (*RP-18*; MeOH/ 0.1% TFA, 1:9 to 8:2) to afford *Fr. 1*–*5*, of which *Fr. 2* was subjected by CC (*Sephadex LH-20*; MeOH; and silica gel; $CHCl_3$/MeOH 30:1 to 8:1) to yield **2** (20 mg), **3** (3 mg), and **5** (7 mg). Then, *Fr. D* was separated by CC (*RP-18*; MeOH/ 0.1% TFA, 1:9 to 8:2) to afford fractions *1*–*4*, of which *Fr. 3* was subjected by CC (*Sephadex LH-20*; MeOH; and silica gel; $CHCl_3$/MeOH 15:1 to 5:1) to yield **1** (5 mg).

Table 2. *[1]H-NMR Data of* **1**, **2**, *and* **3**[1]). At 500 MHz, δ in $CDCl_3$; in ppm, J in Hz.

	1	**2**	**3**
H–C(1)	2.77 (*d*, *J* = 3.5)	3.35 (*d*, *J* = 4.0)	2.74 – 2.79 (*m*)
H–C(2)	1.15 – 1.21 (*m*)	1.44 – 1.49 (*m*)	1.37 – 1.40 (*m*)
H_a–C(3)	1.31 – 1.35 (*m*)	1.56 – 1.60 (*m*)	1.52 – 1.57 (*m*)
H_b–C(3)	1.74 – 1.78 (*m*)	1.98 – 2.03 (*m*)	1.77 – 1.82 (*m*)
H_a–C(4)	1.30 – 1.35 (*m*)	1.53 – 1.60 (*m*)	1.38 – 1.42 (*m*)
H_b–C(4)	1.76 – 1.83 (*m*)	2.00 – 2.03 (*m*)	1.86 – 1.90 (*m*)
H–C(6)	1.44 – 1.47 (*m*)	1.72 – 1.75 (*m*)	1.84 – 1.86 (*m*)
H_a–C(7)		3.40 (br. *d*, *J* = 14.5)	2.74 – 2.82 (*m*)
H_b–C(7)	4.97 (br. *s*)	3.59 (*dd*, *J* = 5.0, 14.5)	3.22 – 3.30 (*m*)
H–C(9)	2.07 – 2.13 (*m*)	2.48 (*t*, *J* = 7.0)	2.12 – 2.18 (*m*)
H_a–C(11)	1.28 – 1.33 (*m*)	1.60 – 1.65 (*m*)	1.56 – 1.59 (*m*)
H_b–C(11)	2.16 – 2.24 (*m*)	2.19 – 2.26 (*m*)	1.82 – 1.86 (*m*)
H_a–C(12)	1.59 – 1.67 (*m*)	1.77 – 1.80 (*m*)	1.55 – 1.59 (*m*)
H_b–C(12)	1.59 – 1.67 (*m*)	1.90 – 1.94 (*m*)	1.83 – 1.86 (*m*)
H_a–C(13)	0.67 – 0.75 (*m*)	0.90 – 0.94 (*m*)	1.42 – 1.46 (*m*)
H_b–C(13)	1.78 – 1.82 (*m*)	2.14 – 2.17 (*m*)	1.84 – 1.88 (*m*)
H_a–C(14)	1.35 – 1.40 (*m*)	1.47 – 1.51 (*m*)	1.24 – 1.27 (*m*)
H_b–C(14)	2.25 – 2.34 (*m*)	2.42 – 2.46 (*m*)	1.81 – 1.85 (*m*)
H_a–C(15)	1.24 – 1.28 (*m*)	1.46 – 1.49 (*m*)	1.68 – 1.71 (*m*)
H_b–C(15)	1.58 – 1.63 (*m*)	1.81 – 1.86 (*m*)	1.83 – 1.86 (*m*)
H_a–C(16)	1.25 – 1.28 (*m*)	1.05 – 1.10 (*m*)	1.21 – 1.26 (*m*)
H_b–C(16)	1.61 – 1.65 (*m*)	1.61 – 1.65 (*m*)	1.68 – 1.72 (*m*)
H_a–C(17)	1.25 – 1.29 (*m*)	1.84 – 1.90 (*m*)	1.30 – 1.33 (*m*)
H_b–C(17)	1.65 – 1.70 (*m*)	2.21 – 2.25 (*m*)	1.79 – 1.83 (*m*)
H–C(18)	1.44 – 1.49 (*m*)	1.23 – 1.28 (*m*)	1.72 – 1.77 (*m*)
Me(19)	0.90 (*d*, *J* = 6.0)	1.06 (*d*, *J* = 6.5)	0.91 (*d*, *J* = 6.5)
Me(20)	0.79 (*d*, *J* = 6.0)	0.95 (*d*, *J* = 6.5)	1.03 (*d*, *J* = 6.5)
Me(21)	0.89 (*s*)	1.08 (*s*)	0.88 (*s*)
H–C(22)	1.51 – 1.55 (*m*)	1.63 – 1.66 (*m*)	3.33 (*dd*, *J* = 2.0, 9.0)
Me(24)	1.18 (*s*)	1.34 (*s*)	1.11 (*s*)
CH_2(25)			3.40 (*dd*, *J* = 16.0, 11.0)
H–C(26)	3.56 (*d*, *J* = 4.0)	3.80 (*d*, *J* = 5.0)	4.16 (*d*, *J* = 7.0)
H_a–C(27)	1.46 – 1.51 (*m*)	1.47 – 1.52 (*m*)	1.94 – 1.98 (*m*)
H_b–C(27)	1.74 – 1.78 (*m*)	1.82 – 1.86 (*m*)	2.03 – 2.07 (*m*)
H_a–C(28)	1.71 – 1.67 (*m*)	1.81 – 1.86 (*m*)	1.73 – 1.77 (*m*)
H_b–C(28)	1.78 – 1.74 (*m*)	1.92 – 1.97 (*m*)	1.95 – 1.98 (*m*)
Me(30)	1.32 (*s*)	1.43 (*s*)	1.46 (*s*)

Yunnandaphninine F (=*(1*S*,2*R*,5*R*)-8-{2-[(3a*R*,9*R*,10b*S*)-Dodecahydro-12-hydroxy-6a-methyl-9-(1-methylethyl)-10a*H*-3a,10,6-(azanetriylmethano)benz[e]azulen-10a-yl]ethyl}-2-hydroxy-1,5-dimethyl-6-oxabicyclo[3.2.1]octan-7-one*; **1**). White powder. $[\alpha]_D^{25} = +8.3$ ($c = 0.28$, $CHCl_3$). IR (KBr): 3459, 2938, 2866, 2870, 1748, 1631, 1455, 1382, 1261. ^{1}H- and ^{13}C-NMR: see the *Tables 2* and *1*. ESI-MS: 486. HR-ESI-MS: 486.3580 ($[M+H]^+$, $C_{30}H_{48}NO_4^+$; calc. 486.3583).

Yunnandaphninine G (=*(1*S*,2*R*,5*R*)-8-{2-[(3a*R*,9*R*,10b*S*)-Dodecahydro-6a-methyl-9-(1-methylethyl)-10a*H*-3a,10,6-(azanetriylmethano)benz[e]azulen-10a-yl]ethyl}-2-hydroxy-1,5-dimethyl-6-oxabicyclo[3.2.1]octan-7-one*; **2**). White powder. $[\alpha]_D^{25} = +16.7$ ($c = 0.45$, $CHCl_3$). IR (KBr): 3419, 2926, 2859, 2870, 1764, 1455, 1384, 1306. ^{1}H- and ^{13}C-NMR: see the *Tables 2* and *1*. ESI-MS: 470. HR-ESI-MS: 470.3627 ($[M+H]^+$, $C_{30}H_{48}NO_3^+$; calc. 470.3634).

Yunnandaphninine H (=*23-[(1S,4S)-1,4-Dimethyl-2,8-dioxabicyclo[3.2.1]oct-4-yl]daphnan-23-ol*; **3**). White powder. $[\alpha]_D^{25} = -1.1$ ($c = 0.47$, $CHCl_3$). IR (KBr): 3421, 2936, 2869, 1736 1630, 1455, 1385, 1227. ^{1}H- and ^{13}C-NMR: see the *Tables 2* and *1*. ESI-MS: 471. HR-ESI-MS: 472.3790 ($[M+H]^+$, $C_{30}H_{50}NO_3^+$; calc. 472.3791).

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