Three New Alkaloids, Paxiphyllines C – E, from *Daphniphyllum paxianum*

by **Yu Zhang**[a][b], **Ying-Tong Di**[a], **Hai-Yang Liu**[a], **Chun-Shun Li**[a], **Cheng-Jian Tan**[a], **Qiang Zhang**[a], **Xin Fang**[a], **Shun-Lin Li**[a], and **Xiao-Jiang Hao***[a]

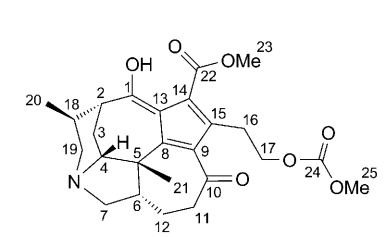
[a]) State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650204, P. R. China (phone: +86-871-5223263; fax: +86-871-5219684; e-mail: haoxj@mail.kib.ac.cn)

[b]) Graduate University of the Chinese Academy of Sciences, Beijing 100049, P. R. China

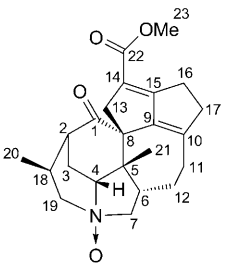
Nine *Daphniphyllum* alkaloids, including three new ones, paxiphyllines C–E (**1**–**3**, resp.), were isolated from the twigs and the leaves of *Daphniphyllum paxianum*. Paxiphylline C (**1**) represents the first example of *Daphniphyllum* alkaloids with a carbonyldioxy group. Their structures were elucidated on the basis of spectroscopic data.

Introduction. – *Daphniphyllum* alkaloids with highly complex polycyclic systems are a group of structurally diverse natural products that were isolated from plants of the genus *Daphniphyllum* [1]. Their unique ring systems have been the attractive targets for total synthesis as well as biosynthetic studies [1–7]. In recent years, many new alkaloids with novel skeletons have been obtained from this genus [3–7]. In the course of a further investigation on the twigs and leaves of *Daphniphyllum paxianum* [3c][3e][5d][5e], three new alkaloids **1**–**3**, namely paxiphyllines C (**1**), D (**2**), and E (**3**), were obtained together with six known ones (**4**–**9**): daphnicyclidin A (**4**) [4], daphnicyclidin B (**5**) [4], longistylumphylline A (**6**) [5a], daphnilongeranin A (**7**) [5b], daphmacrine (**8**) [6], and daphnilactone B (**9**) [1][7]. Herein, we describe the isolation and structure elucidation of the new compounds **1**–**3**.

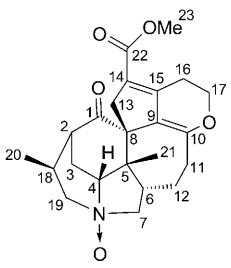
Results and Discussion. – Paxiphylline C (**1**) was obtained as an optically active, light yellow solid. The molecular formula of **1** was established as $C_{25}H_{31}NO_7$ by HR-ESI-MS (*m*/*z* 458.2191 ($[M+H]^+$; calc. 458.2178)), indicating eleven degrees of unsaturation. The UV absorptions at 361 (4.1) and 292 (4.1) nm suggested the presence of a conjugated cyclopentadiene moiety [4][8]. Relevant IR absorptions implied the presence of OH (3427 cm^{-1}) and CO (1745, 1688 cm^{-1}) functionalities. The 1D- and 2D-NMR spectra revealed 25 ^{13}C signals, comprising one quaternary C-atom, and nine trisubstituted sp^2 C-atoms, four sp^3 CH groups, seven sp^3 CH_2 groups, two Me and two MeO groups. The nine trisbustituted sp^2 C-atoms were attributable to two ester C=O groups (δ(C) 175.9 and 155.6), one ketone C=O group at δ(C) 202.7, and three tetrasubstituted C=C bonds (*Table 1*). The NMR spectra also indicated two CH_2 groups (δ(C) 60.2, 54.7) and one CH group (δ(C) 66.4) next to an amino group. Since two ester C=O groups, one ketone C=O group, and three C=C bonds accounted for 6



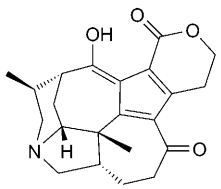
1



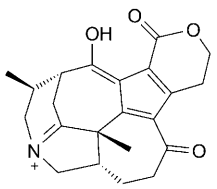
2



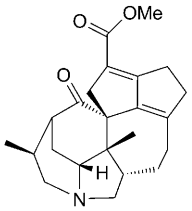
3



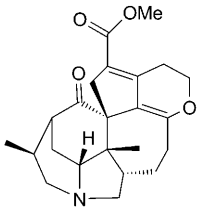
4



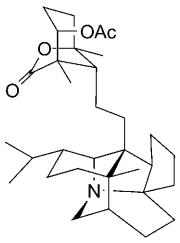
5



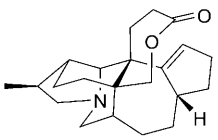
6



7



8



9

Table 1. *^{13}C-NMR Data of* **1**, **2**, *and* **3**. At 100 MHz, δ in $CDCl_3$; in ppm.

	1	**2**	**3**		**1**	**2**	**3**
C(1)	194.6 (*s*)	211.2 (*s*)	211.3 (*s*)	C(14)	120.8 (*s*)	114.4 (*s*)	115.5 (*s*)
C(2)	46.9 (*d*)	41.9 (*d*)	42.3 (*d*)	C(15)	126.9 (*s*)	170.2 (*s*)	148.9 (*s*)
C(3)	17.1 (*t*)	18.2 (*t*)	19.3 (*t*)	C(16)	27.5 (*t*)	25.4 (*t*)	25.0 (*t*)
C(4)	66.4 (*d*)	86.6 (*d*)	88.6 (*d*)	C(17)	69.0 (*t*)	41.9 (*t*)	65.2 (*t*)
C(5)	49.2 (*s*)	48.0 (*s*)	49.2 (*s*)	C(18)	28.8 (*d*)	31.3 (*d*)	31.2 (*d*)
C(6)	47.7 (*d*)	48.7 (*d*)	46.5 (*d*)	C(19)	54.7 (*t*)	67.2 (*t*)	67.6 (*t*)
C(7)	60.2 (*t*)	70.7 (*t*)	69.1 (*t*)	C(20)	16.9 (*q*)	19.5 (*q*)	19.6 (*q*)
C(8)	130.0 (*s*)	59.9 (*s*)	62.5 (*s*)	C(21)	35.2 (*q*)	24.5 (*q*)	23.4 (*q*)
C(9)	129.3 (*s*)	147.5 (*s*)	115.9 (*s*)	C(22)	175.9 (*s*)	165.9 (*s*)	165.5 (*s*)
C(10)	202.7 (*s*)	152.5 (*s*)	162.9 (*s*)	C(23)	52.8 (*q*)	51.1 (*q*)	51.1 (*q*)
C(11)	39.2 (*t*)	25.4 (*t*)	27.5 (*t*)	C(24)	155.6 (*s*)		
C(12)	26.0 (*t*)	24.5 (*t*)	21.7 (*t*)	C(25)	54.5 (*q*)		
C(13)	125.7 (*s*)	45.8 (*t*)	41.9 (*t*)				

out of 11 degrees of unsaturation, the remaining five degrees of unsaturation were assumed to be due to the presence of a pentacyclic system in **1**.

Analysis of the 2D-NMR spectra (including ^{1}H,^{1}H-COSY, HMQC, and HMBC) of **1** established three fragments **a** (C(2) to C(4), and C(18) to C(19) and C(20)), **b** (C(6) to C(7), and to C(12), and C(11) to C(12)), and **c** (C(16) to C(17)) as shown with bold bonds in *Fig. 1*. HMBC Correlations of H–C(7) to C(4) and C(19) suggested that C(4), C(7), and C(19) were connected to each other through a N-atom. Connections between C(4), C(6), and Me(21) *via* C(5) were suggested by HMBC cross-peaks of Me(21) to C(4), C(5), and C(6) and H–C(6) to C(5). In addition, HMBC correlations of CH_2(16) to C(9), C(14), and C(15), CH_2(17) to C(15), and Me(21) to C(8) suggested compound **1** possessing an N-containing pentacyclic skeleton like daphnicyclidin H [4]. Furthermore, one MeO group connected to C(22) was indicated by HMBC correlation of MeO(23) to C(22). HMBC Correlations of MeO(25) and CH_2(17) to C(24) indicated that C(17) and C(25) were connected through a O–CO–O group. Thus, the gross structure of paxiphylline C (**1**), an alkaloid of the daphnicyclidin-type, was elucidated as shown in *Fig. 1*.

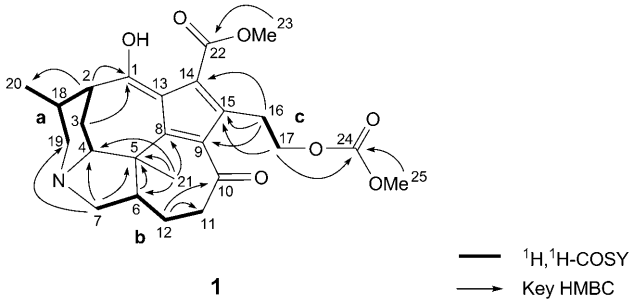


Fig. 1. *Key ^{1}H,^{1}H-COSY and HMBC data of* **1**

The relative configuration of **1** was elucidated by using a ROESY spectrum as shown in the computer-generated 3D drawing (*Fig. 2*). The ROESY correlations H_β–C(7)/H–C(6), H–C(6)/Me(21), Me(21)/H–C(4), and H–C(4)/H_β–C(3), implied that H–C(6), Me(21), and H–C(4) are in β-configuration. The correlations H_β–C(3)/H–C(2) and H_β–C(3)/Me(20) implied that H–C(2) has β-configuration as well.

The molecular formula of paxiphylline D (**2**) was assigned as $C_{23}H_{29}NO_4$ from HR-ESI-MS (*m*/*z* 384.2178 ($[M+H]^+$; calc. 384.2174)), with ten degrees of unsaturation. The IR spectrum was indicative of the presence of a ketone C=O group (1701 cm^{-1}), showing up at δ(C) 211.2 ppm in the ^{13}C-NMR spectrum. The UV absorption at 291 nm (log $\varepsilon = 4.2$) and IR bands at 1663 and 1635 cm^{-1} indicated the presence of an ester C=O group conjugated with two C=C bonds [8]. The ^{1}H- and ^{13}C-NMR data (*Tables 2* and *1*, resp.) of **2** revealed 23 ^{13}C signals corresponding to eight quaternary C-atoms, four CH groups, eight CH_2 groups, and three Me groups.

Comparison of the NMR data of **2** with those of longistylumphylline A [5a], showed that the compounds are closely related, except for significant changes of the chemical shifts of the C-atoms α to the N-atom, namely C(4) (δ(C) 86.6), C(7) (70.7),

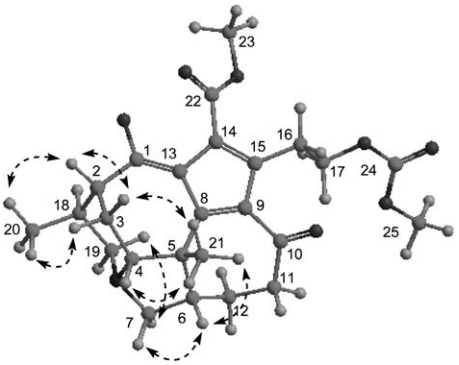


Fig. 2. *Key ROESY correlations of* **1**

Table 2. *^{1}H-NMR Data of* **1**, **2**, *and* **3**. At 400 MHz, δ in $CDCl_3$; in ppm, J in Hz.

	1	**2**	**3**
H–C(2)	2.46–2.51 (*m*)	2.39 (br. *s*)	2.33 (br.)
H_a–C(3)	1.65–1.72 (*m*)	2.16–2.22 (*m*)	
H_b–C(3)	2.11–2.18 (*m*)	2.46–2.52 (*m*)	2.41–2.50 (*m*)
H–C(4)	3.00 (br. *s*)	3.86 (br. *s*)	3.99–4.02 (*m*)
H–C(6)	2.28 (br.)	3.66–3.68 (*m*)	3.24–3.30 (*m*)
H_a–C(7)	2.53–2.59 (*m*)	3.28 (br.)	3.13–3.17 (*m*)
H_b–C(7)	3.93–4.01 (*m*)	3.35–3.39 (*m*)	3.35–3.42 (*m*)
H_a–C(11)		2.02–2.06 (*m*)	1.97–2.03 (*m*)
H_b–C(11)	2.46–2.59 (*m*)	2.14–2.19 (*m*)	2.22–2.29 (*m*)
H_a–C(12)	1.66–1.76 (*m*)	1.82–1.88 (*m*)	1.76–1.83 (*m*)
H_b–C(12)	2.01–2.08 (*m*)	1.92–1.95 (*m*)	1.97–2.05 (*m*)
H_a–C(13)		2.84–2.89 (*m*)	2.72 (*d*, J = 16.8)
H_b–C(13)		3.47 (br. *d*, J = 16.0)	3.26 (*d*, J = 16.8)
H_a–C(16)	2.75–2.83 (*m*)		2.69–2.76 (*m*)
H_b–C(16)	3.38–3.43 (*m*)	2.69–2.74 (*m*)	3.09–3.15 (*m*)
H_a–C(17)	4.01–4.05 (*m*)	2.88 (br. *d*, J = 17.6)	3.97 (*ddd*, J = 10.8, 10.8, 3.6)
H_b–C(17)	4.06–4.11 (*m*)	2.96 (br. *d*, J = 17.6)	4.18 (*ddd*, J = 10.8, 5.2, 5.2)
H–C(18)	2.24–2.31 (*m*)	2.47–2.55 (*m*)	2.54–2.60 (*m*)
H_a–C(19)	3.11 (br. *d*, J = 11.9)		3.14 (*dd*, J = 13.8, 4.8)
H_b–C(19)	3.56–3.63 (*m*)	3.18 (*dd*, J = 15.6, 9.2)	3.62 (*dd*, J = 13.8, 7.3)
Me(20)	1.29 (*d*, J = 7.0)	1.21 (*d*, J = 6.6)	1.16 (*d*, J = 6.7)
Me(21)	0.99 (*s*)	1.37 (*s*)	1.42 (*s*)
MeO(23)	3.74 (*s*)	3.68 (*s*)	3.70 (*s*)
MeO(25)	3.60 (*s*)		

and C(19) (67.2) which resonated at lower field than those of longistylumphylline A (C(4) (δ(C) 64.4), C(7) (54.1), and C(19) (49.7)), indicating that paxiphylline D (**2**) is the N-oxide form of longistylumphylline A.

Paxiphylline E (**3**) has the molecular formula $C_{23}H_{29}NO_5$ as determined by HR-ESI-MS (*m*/*z* 400.2134 ($[M+H]^+$, calc. 400.2123)). IR Absorption bands at 1703 and 1626 cm^{-1} indicated the presence of C=O- and C=C-functionalities. In accordance with the molecular formula, the presence of eight quaternary C-atoms, four CH groups,

eight CH_2 groups, and three Me groups was revealed by analyses of its ^{1}H- and ^{13}C-NMR data (*Tables 2* and *1*, resp.). A comparison of the ^{13}C chemical shifts of C(4), C(7), and C(19) (δ(C) 88.6, 69.1, and 67.6, resp.) in **3** with those of daphnilongeranine A (**7**) (δ(C) 67.2, 55.7, and 51.0, resp.) [5b], indicated the presence of an N-oxide group attached to these C-atoms. Thus, paxiphylline E (**3**) was implied to be the N-oxide form of daphnilongeranine A (**7**), which was further substantiated through 2D-NMR experiments, including ^{1}H,^{1}H-COSY, HMQC, HMBC, and ROESY spectra.

The known alkaloids daphnicyclidin A (**4**), daphnicyclidin B (**5**), longistylumphylline A (**6**), daphnilongeranin A (**7**), daphmacrine (**8**), and daphnilactone B (**9**) were identified on the basis of their reported spectral data (ESI-MS, ^{1}H- and ^{13}C-NMR), compared with our values [1][4][5a][5b][6][7].

The cytotoxic activities of compounds **1**–**3** against the growth of tumor cell lines (P-388 (mouse lymphocytic leukemia) and A549 (human lung adenocarcinoma)) were evaluated. The results indicated that all the three alkaloids were inactive against the above cancer cell lines (50% effective dose of clonal inhibition (ED_{50}) > 10 μg/ml).

Experimental Part

General. TLC: SiO_2 plates; visualization by *Dragendorff*'s reagent. Column chromatography (CC): Silica gel *H* (SiO_2; 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 discs, 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 Me_4Si as internal standard, *J* in Hz. ESI-MS: *Finnigan MAT 90* instrument; in *m*/*z*. HR-ESI-MS: *API Qstar Pulsar LC*/*TOF* instrument.

Plant Material. The twigs and the leaves of *Daphniphyllum paxianum* were collected in Sichuan Province, P. R. China, in July 2005. The material was identified by Associate Prof. *Zhaoyang Zhang*, and a specimen was deposited with the State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences.

Extraction and Isolation. The air dried and powdered twigs and leaves of *D. paxianum* (20.0 kg) were extracted with 95% EtOH, and the crude extract was adjusted with sat. tartaric acid to pH *ca.* 2. The acidic mixture was defatted with petroleum ether (PE), and then extracted with $CHCl_3$. The aq. phase was basified to pH *ca.* 10 with sat. Na_2CO_3, and extracted with $CHCl_3$ to obtain the crude alkaloid fraction (16.0 g). This material was subjected to SiO_2 CC with $CHCl_3$/MeOH (1:0 → 0:1) to obtain five major fractions (*Fr. A*–*E*). *Fr. B* (3.0 g), eluted with $CHCl_3$/MeOH 30:1 and PE/Et_2NH (30:1 → 5:1), afforded **2** (8 mg), **3** (9 mg), **6** (7 mg), **7** (10 mg), **8** (7 mg), and **9** (10 mg). *Fr. D* (2.3 g) was purified by CC (C_{18} reversed-phase silica gel, MeOH/H_2O 4:6) to give **1** (16 mg), **4** (25 mg), and **5** (17 mg).

Paxiphylline C (= *Methyl (6a*S,*11*R,*12b*S*)-5,6,6a,7,9,10,11,12,12a,12b-Decahydro-13-hydroxy-3-{2-[(methoxycarbonyl)oxy]ethyl}-10,12b-dimethyl-4-oxo-4*H-*11,1-(metheno)azuleno[4,5-*a*]indolizine-2-carboxylate*; **1**). Light yellow solid. $[\alpha]_D^{18} = -11.8$ ($c = 0.23$, MeOH). UV (MeOH): 361 (4.1), 292 (4.1). IR (KBr): 3427, 2928, 1745, 1688, 1553, 1440, 1424, 1354, 1270, 1165, 1077, 944. ^{1}H- and ^{13}C-NMR: *Tables 2* and *1*, resp. ESI-MS: 458.3 ($[M+H]^+$). HR-ESI-MS: 458.2191 ($[M+H]^+$, $C_{25}H_{32}NO_7^+$; calc. 458.2178).

Paxiphylline D (= *Methyl (4a*S,*8*S,*10a*R,*10b*S,*10c*R*)-2,3,4,4a,5,7,8,9,10,10a,10b,11-Dodecahydro-8,10b-dimethyl-13-oxo-1*H-*9,10c-methanocyclopenta[1,8]azuleno[4,5-*a*]indolizine-12-carboxylate 6-Oxide*; **2**). Colorless oil. $[\alpha]_D^{25} = -91.0$ ($c = 0.50$, MeOH). UV (MeOH): 291 (4.2). IR (KBr): 2925, 1701, 1663, 1635, 1437, 1352, 1262, 1120, 1062. ^{1}H- and ^{13}C-NMR: *Tables 2* and *1*, resp. ESI-MS: 384.4 ($[M+H]^+$). HR-ESI-MS: 384.2178 ($[M+H]^+$, $C_{23}H_{30}NO_4^+$; calc. 384.2174).

Paxiphylline E (= *Methyl (5a*S*,9*S*,11a*R*,11b*S*,11c*S*)-1,4,5,5a,6,8,9,10,11,11a,11b,12-Dodecahydro-9,11b-dimethyl-14-oxo-2*H*-10,11c-methanopyrano[4′,3′,2′:1,8]azuleno[4,5-*a*]indolizine-13-carboxylate 7-Oxide*; **3**). Colorless solid. $[\alpha]_D^{21} = -42.9$ ($c = 0.14$, MeOH). UV (MeOH): 321 (4.0). IR (KBr): 3430 (H_2O), 2924, 1703, 1626, 1437, 1259, 1129, 1069, 1000. ^{1}H- and ^{13}C-NMR: *Tables 2* and *1*, resp. ESI-MS: 400.3 ($[M+H]^+$). HR-ESI-MS: 400.2134 ($[M+H]^+$, $C_{23}H_{30}NO_5^+$; calc. 400.2123).

The Financial support of the *National Science Foundation* (No. 20672120) of P. R. China is gratefully acknowledged. We thank Associate Prof. *Zhaoyang Zhang*, Kunming Institute of Botony, Chinese Academy of Sciences (CAS), for the collection and identification of the plant material.

REFERENCES

[1] J. Kobayashi, H. Morita, in 'The Alkaloids', Ed. G. A. Cordell, Academic Press, New York, 2003, Vol. 60, p. 165.

[2] G. A. Wallence, C. H. Heathcock, *J. Org. Chem*. **2001**, *66*, 450; C. H. Heathcock, *Proc. Natl. Acad. Sci. U.S.A*. **1996**, *93*, 14323; C. H. Heathcock, D. Joe, *J. Org. Chem.* **1995**, *60*, 1131; C. H. Heathcock, *Angew. Chem., Int. Ed*. **1992**, *31*, 665.

[3] a) Q. Zhang, Y.-T. Di, H.-Y. Liu, N.-C. Kong, S. Gao, C.-S. Li, Y. Zhang, S.-L. Li, X.-J. Hao, *Helv. Chim. Acta* **2008**, *91*, 914; b) Y.-T. Di, L.-L. Liu, C.-S. Li, Y. Zhang, Q. Zhang, S.-Z. Mu, Q.-Y. Sun, F.-M. Yang, H.-Y. Liu, X.-J. Hao, *Helv. Chim. Acta* **2008**, *91*, 838; c) S.-Z. Mu, J.-S. Wang, X.-S. Yang, H.-P. He, C.-S. Li, Y.-T. Di, Y. Wang, Y. Zhang, X. Fang, L.-J. Huang, X.-J. Hao, *J. Nat. Prod*. **2008**, *71*, 564; d) C. Tan, Y. Di, Y. Wang, Y. Wang, S. Mu, S. Gao, Y. Zhang, N. Kong, H. He, J. Zhang, X. Fang, C. Li, Y. Lu, X. Hao, *Tetrahedron Lett*. **2008**, *49*, 3376; e) Y. Zhang, H. He, Y. Di, S. Mu, Y. Wang, J. Wang, C. Li, N. Kong, S. Gao, X. Hao, *Tetrahedron Lett*. **2007**, *48*, 9104; f) S.-Z. Mu, C.-S. Li, H.-P. He, Y.-T. Di, Y. Wang, Y.-H. Wang, Z. Zhang, Y. Lu, L. Zhang, X.-J. Hao, *J. Nat. Prod*. **2007**, *70*, 1628; g) N.-C. Kong, H.-P. He, Y.-H. Wang, S.-Z. Mu, Y.-T. Di, X.-J. Hao, *J. Nat. Prod*. **2007**, *70*, 1348; h) N.-C. Kong, H.-P. He, Y.-H. Wang, S. Gao, Y.-T. Di, X.-J. Hao, *Helv. Chim. Acta* **2007**, *90*, 972; i) C.-S. Li, Y.-T. Di, H.-P. He, S. Gao, Y.-H. Wang, Y. Lu, J.-L. Zhong, X.-J. Hao, *Org. Lett*. **2007**, *9*, 2509; j) Y.-T. Di, H.-P. He, Y.-S. Wang, L.-B. Li, Y. Lu, J.-B. Gong, X. Fang, N.-C. Kong, S.-L. Li, H.-J. Zhu, H.-J. Hao, *Org. Lett*. **2007**, *9*, 1355; k) S.-Z. Mu, X.-W. Yang, Y.-T. Di, H.-P. He, Y. Wang, Y.-H. Wang, L. Li, X.-J. Hao, *Chem. Biodivers.* **2007**, *4*, 129; l) C. Li, H. He, Y. Di, Y. Wang, S. Mu, S. Li, S. Gao, Z. Gao, X. Hao, *Tetrahedron Lett*. **2007**, *48*, 2737; m) Y.-T. Di, H.-P. He, C.-S. Li, J.-M. Tian, S.-Z. Mu, S.-L. Li, S. Gao, X.-J. Hao, *J. Nat. Prod*. **2006**, *69*, 1745; n) Y.-T. Di, H.-P. He, Y. Lu, P. Yi, L. Li, L. Wu, X.-J. Hao, *J. Nat. Prod*. **2006**, *69*, 1074; o) S.-Z. Mu, Y. Wang, H.-P. He, X.-W. Yang, Y.-H. Wang, Y.-T. Di, Y. Lu, Y. Chang, X.-J. Hao, *J. Nat. Prod*. **2006**, *69*, 1065.

[4] J. Kobayashi, Y. Inaba, M. Shiro, N. Yoshida, H. Morita, *J. Am. Chem. Soc.* **2001**, *123*, 11402.

[5] a) X. Chen, Z.-J. Zhan, J.-M. Yue, *Helv. Chim. Acta* **2005**, *88*, 854; b) S.-P. Yang, H. Zhang, C.-R. Zhang, H.-D. Cheng, J.-M. Yue, *J. Nat. Prod*. **2006**, *69*, 79; c) S.-P. Yang, J.-M. Yue, *J. Org. Chem*. **2003**, *68*, 7961; d) Z.-J. Zhan, S.-P. Yang, J.-M. Yue, *J. Org. Chem*. **2004**, *69*, 1726; e) S.-P. Yang, J.-M. Yue, *Org. Lett*. **2004**, *6*, 1401.

[6] T. Nakano,Y. Saeki, *Tetrahedron Lett*. **1967**, *8*, 4791.

[7] H. Morita, N. Yoshida, J. Kabayashi, *Tetrahedron* **2000**, *56*, 2641.

[8] S. Yamamura, Y. Hirata, *Tetrahedron Lett*. **1974**, *15*, 2849.

Received May 16, 2008