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Lycochininines A–C, novel $C_{27}N_3$ alkaloids from *Lycopodium chinense*

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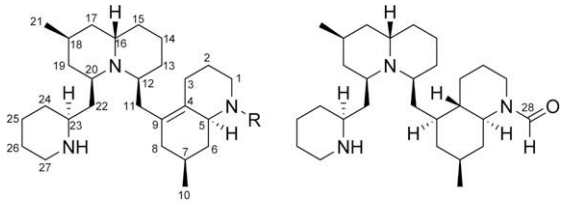
ABSTRACT

Three novel $C_{27}N_3$-type *Lycopodium* alkaloids, lycochininines A–C (**1**–**3**) consisting of an octahydroquinoline or a decahydroquinoline, a quinolizidine, and a piperidine, were isolated from the club moss *Lycopodium chinense*. The relative stereochemistry of **1**–**3** was determined by a combination of NOESY correlations and chemical transformations.

Lycopodium alkaloids[1] with unique heterocyclic frameworks of $C_{11}N$, $C_{16}N$, $C_{16}N_2$, and $C_{27}N_3$ types have attracted great interest from biogenetic[1,2] and biological[3] points of view. A common feature in all *Lycopodium* alkaloids is a polycyclic carbon skeleton with varying levels of oxidation. These unique skeletons have also been challenging targets for total synthesis.[4] Among them, huperzine A is a highly specific and potent inhibitor of acetylcholinesterase (AChE).[3] Recently, we isolated new types of polycyclic alkaloids from various *Lycopodium* species.[5–11] Our interest has been focused on isolation of structurally interesting alkaloids and biosynthetic intermediates to clarify the biogenetic pathway. Further investigation on extracts of *L. chinense* H. Christ (Lycopodiaceae) resulted in the isolation of novel $C_{27}N_3$ alkaloids, lycochininines A–C (**1**–**3**). This Letter describes the isolation and structure elucidation of **1**–**3**.



1 : R = $^{28}CH_3$
2 : R = H

3

The club moss *L. chinense* collected in Hokkaido was extracted with MeOH, and the extract was partitioned between EtOAc and 3% aqueous tartaric acid. Water-soluble materials, adjusted to pH 9 with saturated Na_2CO_3 aq, were extracted with $CHCl_3$. The $CHCl_3$-soluble materials were subjected to an LH-20 column ($CHCl_3$/MeOH, 1:1), followed by an amino silica gel column (hexane/EtOAc→$CHCl_3$/MeOH) and then a silica gel column ($CHCl_3$/MeOH/TFA) to afford lycochininines A (**1**, 0.0002%), B (**2**, 0.0005%), and C (**3**, 0.0005%) together with the known $C_{22}N_2$-type alkaloids, senepodines A and E.[12–14]

Lycochinine A (**1**),[15] colorless amorphous solid, $[\alpha]_D^{23}$ −15 (*c* 1.0, MeOH), showed a molecular formula, $C_{28}H_{49}N_3$, which was determined by HRESITOFMS [*m/z* 428.3993 $(M+H)^+$, Δ −1.2 mmu], indicating 6 degrees of unsaturation. IR absorption band was characteristic of amino (3400 cm^{-1}) group. ^1H and ^{13}C NMR data (Table 1) suggested the presence of 16 sp^3 methylenes, seven sp^3 methines, three methyls, and two sp^2 quaternary carbons. Among them, two sp^3 methylenes (δ_C 57.2, δ_H 3.09, 3.45; δ_C 46.2, δ_H 2.95, 3.34) and five sp^3 methines (δ_C 66.7, δ_H 3.67; δ_C 55.0, δ_H 3.62; δ_C 54.2, δ_H 3.72; δ_C 53.3, δ_H 3.79; δ_C 55.4, δ_H 3.17), and one methyl (δ_C 41.4, δ_H 2.81) were attached to the nitrogen atom. Since only one of six unsaturations was accounted for, **1** was inferred to possess 5 rings. Partial structures **a** (C-1–C-3), **b** (C-5–C-8 and C-10), and **c** (C-11–C-27) were deduced from detailed analyses of the 2D NMR data (^1H–^1H COSY, HOHAHA, HMQC, and HMQC–TOCSY spectra) of **1** (Fig. 1). The connection among partial structures **a**, **b**, **c**, and the tetra-substituted olefinic carbons, and construction of an *N*-methyloctahydro-quinoline ring (C-1–C-9 and N-1) were deduced from the HMBC correlations of H_2-8 to C-4, C-9, and C-11, H-3a to C-4, and H_3-28 to C-1 and C-5. The presence of a piperidine ring (C-23–C-27, and N-3) was elucidated from the HMBC correlation of H-27b to C-23. HMBC correlations from H-12 to C-16 and H-16 to C-20 in partial structure **c** established the connection among C-12, C-16, and C-20 through a nitrogen atom, constructing the quinolizidine ring (C-12–C-20 and N-2). Thus, the gross structure of lycochinine A was assigned as **1**, consisting of an octahydroquinoline, a quinolizidine, and a piperidine with three methyls at C-7, C-18, and N-1.

The relative stereochemistry in **1** was deduced from NOESY data and ^3J coupling constants (Fig. 2). In the octahydroquinoline moiety (C-1–C-9 and N-1), five NOESY correlations (H-1a/H-3a, H-1a/H-5, H-3a/H-5, H-5/H-7, and H-6a/H-8a) were observed. These correlations indicated that each six-membered ring took a pseudo-chair form and the methyl group at C-7 was oriented equatorially. Three

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Table 1
^{1}H and ^{13}C NMR data of lycochinines A–C (**1**–**3**) in CD_3OD

	1[a]		**2**[b]		**3**[c]	
1a	3.09 (1H, dd, 13.2, 12.8)	57.2	3.11 (1H, ddd,13.9, 12.9, 2.9)	45.4	2.52 (1H, ddd, 12.9, 12.9, 2.8)	43.1
1b	3.45 (1H, br d, 12.8)		3.39 (1H, br d, 13.9)		4.52 (1H, br d, 12.9)	
2a	1.69 (1H, m)	24.5	1.64 (1H, m)		1.42 (1H, m)	26.8
2b	2.00 (1H, m)		2.01 (1H, m)	24.2	1.78 (1H, m)	
3a	2.03 (1H, m)	27.5	2.07 (1H, m)		1.14 (1H, m)	30.6
3b	2.94 (1H, m)		2.92 (1H, br d, 13.7)	27.0	2.24 (1H, br d, 11.3)	
4		128.2[d]			0.94 (1H, dddd, 10.6, 10.6, 10.6, 3.1)	49.5
5	3.67 (1H, m)	66.7	3.82 (1H, m)	128.2[d]	3.01 (1H, m)	63.8
6a	1.26 (1H, ddd, 11.6, 11.6, 11.6)	36.1	1.26 (1H, m)	57.7	1.34 (1H, ddd, 11.8, 11.8, 11.8)	38.4
6b	2.31 (1H, m)		2.11 (1H, m)	37.0	2.02 (1H, br d, 11.8)	
7	1.70 (1H, m)	29.0	1.75 (1H, m)		1.53 (1H, m)	32.7
8a	1.93 (1H, m)	39.8	1.95 (1H, m)	28.5	0.72 (1H, ddd, 12.3, 12.3, 12.3)	42.4
8b	2.02 (1H, m)		2.03 (1H, m)	39.7	1.82 (1H, m)	
9		135.9[d]			1.28 (1H, dddd, 10.7, 10.7, 10.6, 3.0)	40.2
10	1.06 (3H, d, 6.6)	21.7	1.04 (3H, d, 6.5)	134.5[d]	1.01 (3H, d, 6.6)	22.9
11a	2.36 (1H, br d, 12.6)	35.3	2.32 (1H, m)	21.6	1.07 (1H, dd, 13.8, 10.7)	35.3
11b	2.97 (1H, br t, 12.6)		3.08 (1H, m)	34.3	2.07 (1H, ddd, 13.8, 7.5, 3.0)	
12	3.62 (1H, m)	55.0	3.74 (1H, m)		3.22 (1H, m)	51.3
13a	1.41 (1H, m)	21.8[e]	1.47 (1H, m)	55.0	1.08 (1H, m)	22.7
13b	1.81 (1H, m)		1.83 (1H, m)	25.6[e]	1.78 (1H, m)	
14a	1.74 (1H, m)	19.2	1.74 (1H, m)		1.64 (1H, br d, 11.8)	21.3
14b	1.76 (1H, m)		1.80 (1H, m)	18.9	1.77 (1H, m)	
15a	1.53 (1H, m)	25.4	1.57 (1H, m)		1.05 (1H, m)	24.7
15b	2.06 (1H, m)		2.11 (1H, m)	25.4	1.95 (1H, dddd, 12.8, 12.8, 12.8, 4.6)	
16	3.72 (1H, m)	54.2	3.82 (1H, m)		3.16 (1H, br d, 12.8)	51.4
17a	1.48 (1H, m)	37.6	1.56 (1H, m)	57.7	1.26 (1H, ddd, 12.7, 12.7, 5.1)	40.9
17b	1.81 (1H, m)		1.79 (1H, m)	37.8	1.47 (1H, dd, 13.4, 3.3)	
18	1.93 (1H, m)	25.1	1.93 (1H, m)		1.69 (1H, m)	26.4
19a	1.16 (1H, ddd, 13.0, 12.2, 12.2)	39.3	1.20 (1H, m)	24.8	0.84 (1H, ddd, 12.0, 12.0, 12.0)	43.5
19b	2.08 (1H, br d, 13.0)		2.15 (1H, m)	39.2	1.77 (1H, m)	
20	3.79 (1H, br t, 9.6)	53.3	3.90 (1H, m)		3.07 (1H, m)	49.9
21	0.98 (3H, d, 6.6)	21.9	0.97 (3H, d, 6.4)	53.3	0.86 (3H, d, 6.4)	22.9
22a	1.63 (1H, m)	37.6	1.68 (1H, m)	21.8	1.16 (1H, ddd, 14.0, 8.6, 5.4)	43.2
22b	2.23 (1H, ddd, 13.5, 9.9, 4.0)		2.32 (1H, m)	37.0	1.73 (1H, m)	
23	3.17 (1H, dd, 9.9, 9.6)	55.4	3.24 (1H, m)		2.56 (1H, m)	56.3
24a	1.52 (1H, m)	31.9	1.57 (1H, m)	54.8	1.05 (1H, m)	33.2
24b	1.93 (1H, m)		1.93 (1H, m)	31.7	1.76 (1H, m)	
25a	1.64 (1H, m)	24.0	1.62 (1H, m)		1.40 (1H, m)	25.5
25b	1.85 (1H, m)		1.89 (1H, m)	23.5	1.80 (1H, m)	
26a	1.63 (1H, m)	23.6	1.64 (1H, m)		1.44 (1H, m)	26.8
26b	1.88 (1H, m)		1.87 (1H, m)	23.7	1.62 (1H, br d, 12.6)	
27a	2.95 (1H, ddd, 12.6, 12.6, 2.4)	46.2	2.97 (1H, m)		2.62 (1H, ddd, 12.1, 12.1, 2.4)	47.7
27b	3.34 (1H, m)		3.37 (1H, m)	46.1	3.02 (1H, m)	
28	2.81 (3H, s)	41.4			8.13 (1H, s)	160.8

[a] TFA salt recorded at 323 K.
[b] TFA salt recorded at 303 K.
[c] Free base recorded at 293 K.
[d] Assigned by HMBC.
[e] Assigned by HSQC.

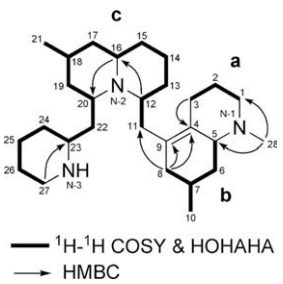

Figure 1. Selected 2D NMR correlations for lycochinine A (**1**).

NOESY correlations (H-15b/H-18 and H-20, and H-18/H-20) were observed in the quinolizidine moiety (C-12–C-20 and N-2). These correlations supported the cis-bis-chair conformation of the quinolizidine ring and both C-21 and C-22 were oriented equatorially against piperidine ring (C-16–C-20 and N-2). Therefore, the two stereochemistries, (5*S**, 7*S**, 12*S**, 16*S**, 18*S**, 20*R**) and (5*R**, 7*R**, 12*S**, 16*S**, 18*S**, 20*R**) were proposed for the relationship between the octahydroquinoline and the quinolizidine rings. Of the two relative stereochemistries, only the former was satisfied by the NOESY correlations of H-8a/H-12, H-8b/H-11a, H-11a/H-12, and H-11b/H-16. The large vicinal coupling constant (12.6 Hz) supported the antiperiplanar relationship between H-12 and H-11b. Furthermore, the relative stereochemistry between the quinolizidine and piperidine rings could be deduced by NOESY correlations for H-12/H-22b, H-19a/H-22a, H-19b/H-23, H-20/H-22b, H-22a/H-23, H-22a/H-24b, and H-23/H-27, as shown in Figure 2. The large coupling constants between H-20 and H-22a (9.6 Hz), and between H-23 and H-24a (9.6 Hz) also supported the rigid solution conformation of **1** and antiperiplanar relationship, respectively. Thus, the structure of lycochinine A (**1**) was assigned as shown.

Lycochinine B (**2**),[16] colorless amorphous solid, $[\alpha]_D^{23}$ −5 (*c* 1.0, MeOH), showed molecular formula, $C_{27}H_{47}N_3$, which was determined by HRESITOFMS [*m*/*z* 414.3843 $(M+H)^+$, Δ −0.5 mmu], less than that of **1** by a CH_2 unit. An IR absorption band (3400 cm^{-1}) was characteristic of amino group. ^{1}H and ^{13}C NMR data of **2** (Table 1) were analogous to those of **1** without the *N*(1)-Me. The

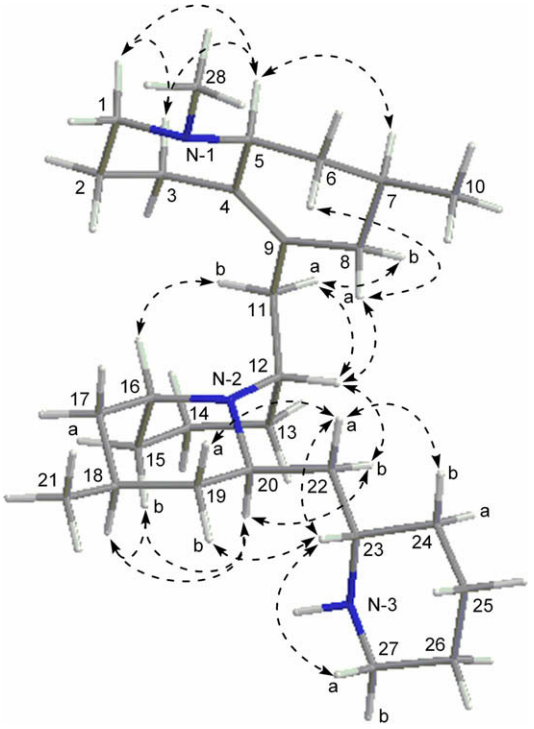

Figure 2. Selected NOESY correlations for lycochinine A (**1**).

gross structure of **2** was elucidated by 2D NMR (^{1}H–^{1}H COSY, HOHAHA, HMQC, and HMBC) data to be the N-1 demethyl form of **1**. Treatment of both **1** and **2** with HCHO and HCOOH afforded an *N*-methyl derivative of **1**, whose spectroscopic data and specific rotation were identical with each other and confirmed the relative configuration of **2**.

Lycochinine C (**3**)[17] showed the pseudomolecular ion peak at *m/z* 444 $(M+H)^+$ in the ESIMS, and the molecular formula, $C_{28}H_{49}N_3O$, was established by HRESIMS [*m/z* 444.3940 $(M+H)^+$ Δ −0.8 mmu], larger than **2** by a CH_2O unit. ^{1}H and ^{13}C NMR spectra of **3** were analogous to those of **2**, although an *N*-formyl group (δ_C 160.8) and two sp^3 methines (δ_C 40.2 and 49.5) in place of a tetrasubstituted olefin carbons (δ_C 128.2 and 134.5) of **2** were observed for **3**.

The ^{1}H–^{1}H COSY and HOHAHA spectra revealed connectivities as shown by the bold line. (Fig. 3) Each connection through a nitrogen atom was elucidated by HMBC correlation of H-1 to C-5, H-12 to C-16, H-16 to C-20, H-27 to H-23, and H-28 to C-1. Thus, the gross structure of lycochinine C was assigned as **3**, consisting of a decahydroquinoline, a quinolizidine, and a piperidine.

The relative configuration of **3** was deduced from NOESY correlations (Fig. 4). The presence of nine NOESY correlations (H-12/H-22b, H-15/H-18, H-15/H-20, H-18/H-20, H-19a/H-22a, H-19b/H-23, H-20/H-22b, H-22a/H-23, H-22a/H-24b, and H-23/H-27a) between the quinolizidine and the piperidine rings was the same as

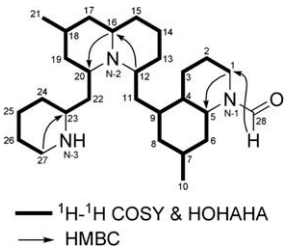

Figure 3. Selected 2D NMR correlations for lycochinine C (**3**).

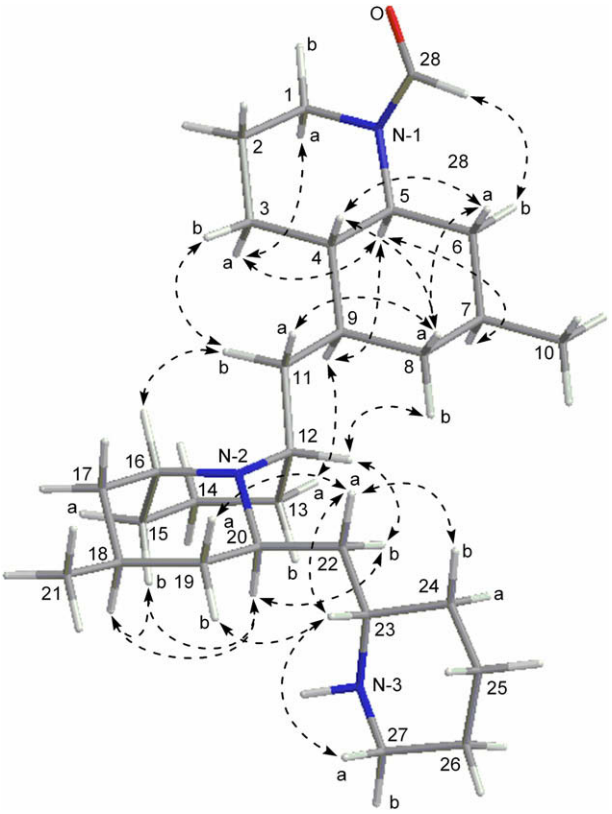

Figure 4. Selected NOESY correlations for lycochinine C (**3**).

those in **1**. In the decahydroquinoline ring (C-1–C-9 and N-1), eight NOESY correlations (H-1a/H-3a, H-1a/H-5, H-3a/H-5, H-4/H-6a, H-4/H-8a, H-5/H-7, H-5/H-9, and H-6a/H-8a) were observed. These correlations indicated that the junction of the decahydroquinoline ring was trans and a methyl group at C-7 was oriented equatorially. The conformation between the quinolizidine ring and the decahydroquinoline ring through a C-11 methylene was deduced from the NOESY cross-peaks of H-3/H-11b, H-8a/H-11a, H-8b/H-12, H-9/H-13a, and H-11b/H-16. The large coupling constants between H-9 and H-11a (10.7 Hz), and between H-11b and H-12 (7.5 Hz) also supported the rigid conformation around the C-11 methylene. Thus, the relative stereochemistry of lycochinine C (**3**) was assigned as shown.

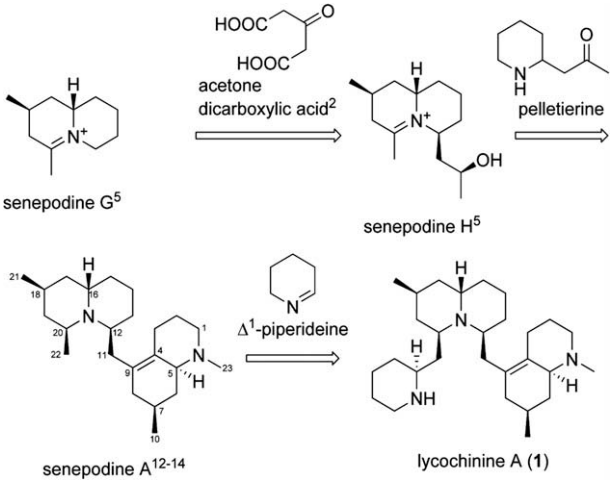

Figure 5. Plausible biogenetic pathway for lycochinine A (**1**).

Lycochinines A–C (**1**–**3**) are a new class of $C_{27}N_3$ *Lycopodium* alkaloids, consisting of an octahydroquinoline or a decahydroquinoline, a quinolizidine ring, and a piperidine ring. A plausible biogenetic pathway for lycochinine A (**1**) is proposed in Figure 5. Lycochinines A–C (**1**–**3**) might be generated from a piperidine unit and senepodine A[12,13] derived from pelletierine via senepodines G[5] and H[5].

Lycochinine C (**3**) showed moderate cytotoxicity against human blood premyelocytic leukemia (HL-60, 46% inhibition at 100 μM), whereas lycochinines A (**1**) and B (**2**) did not show.

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References and notes

1. For reviews of the *Lycopodium* alkaloids, see: (a) Kobayashi, J.; Morita, H. In *The Alkaloids*; Cordell, G. A., Ed.; Academic Press: New York, 2004; Vol. 61, p 1; (b) Ayer, W. A.; Trifonov, L. S. In *The Alkaloids*; Cordell, G. A., Brossi, A., Eds.; Academic Press: New York, 1994; Vol. 45, p 233; (c) Ayer, W. A. *Nat. Prod. Rep.* **1991**, *8*, 455; (d) MacLean, D. B. In *The Alkaloids*; Brossi, A., Ed.; Academic Press: New York, 1985; Vol. 26, p 241; (e) MacLean, D. B.. In *The Alkaloids*; Manske, R. H. F., Ed.; Academic Press: New York, 1973; Vol. 14, p 348; (f) MacLean, D. B. In *The Alkaloids*; Manske, R. H. F., Ed.; Academic Press: New York, 1968; Vol. 10, p 305.
2. (a) Hemscheidt, T.; Spenser, I. D. *J. Am. Chem. Soc.* **1996**, *118*, 1799–1800; (b) Hemscheidt, T.; Spenser, I. D. *J. Am. Chem. Soc.* **1993**, *115*, 3020–3021.
3. Liu, J. S.; Zhu, Y. L.; Yu, C. M.; Zhou, Y. Z.; Han, Y. Y.; Wu, F. W.; Qi, B. F. *Can. J. Chem.* **1986**, *64*, 837–839.
4. (a) Yen, C.-F.; Liao, C.-C. *Angew. Chem., Int. Ed.* **2002**, *41*, 4090–4093; (b) Cassayre, J.; Gagosz, F.; Zard, S. Z. *Angew. Chem., Int. Ed.* **2002**, *41*, 1783–1785; (c) Sha, C.-K.; Lee, F.-K.; Chang, C.-J. *J. Am. Chem. Soc.* **1999**, *121*, 9875–9876; (d) Williams, J. P.; St. Laurent, D. R.; Friedrich, D.; Pinard, E.; Roden, B. A.; Paquette, L. A. *J. Am. Chem. Soc.* **1994**, *116*, 4689–4696; (e) Hirst, G. C.; Johnson, T. O.; Overman, L. E. *J. Am. Chem. Soc.* **1993**, *115*, 2992–2993. and references cited therein.
5. Morita, H.; Hirasawa, Y.; Shinzato, T.; Kobayashi, J. *Tetrahedron* **2004**, *60*, 7015–7023.
6. Koyama, K.; Morita, H.; Hirasawa, Y.; Yoshinaga, M.; Hoshino, T.; Obara, Y.; Nakahata, N.; Kobayashi, J. *Tetrahedron* **2005**, *61*, 3681–3690.
7. Hirasawa, Y.; Morita, H.; Kobayashi, J. *Org. Lett.* **2006**, *8*, 123–126.
8. Hirasawa, Y.; Kobayashi, J.; Obara, Y.; Nakahata, N.; Kawahara, N.; Goda, Y.; Morita, H. *Heterocycles* **2006**, *68*, 2357–2364.
9. Choo, C.; Hirasawa, Y.; Karimata, C.; Koyama, K.; Sekiguchi, M.; Kobayashi, J.; Morita, H. *Bioorg. Med. Chem.* **2007**, *15*, 1703–1707.
10. Hirasawa, Y.; Kato, E.; Kobayashi, J.; Kawahara, N.; Goda, Y.; Shiro, M.; Morita, H. *Bioorg. Med. Chem.* **2008**, *16*, 6167–6171.
11. Hirasawa, Y.; Tanaka, T.; Kobayashi, J.; Kawahara, N.; Goda, Y.; Morita, H. *Chem. Pharm. Bull.* **2008**, *56*, 1473–1476.
12. Morita, H.; Hirasawa, Y.; Yoshida, N.; Kobayashi, J. *Tetrahedron Lett.* **2001**, *42*, 4199–4201.
13. Hirasawa, Y.; Morita, H.; Kobayashi, J. *Tetrahedron* **2003**, *59*, 3567–3573.
14. *Senepodine A TFA salt*: ^{1}H NMR (CD_3OD) δ 3.20 (1H, ddd, 12.7, 12.7, 2.6, H-1), 3.54 (1H, br d, 12.7, H-1), 1.71 (1H, m, H-2), 2.06 (1H, m, H-2), 2.06 (1H, m, H-3), 2.97 (1H, br d, 14.8, H-3), 3.80 (1H, m, H-5), 1.30 (1H, ddd, 12.4, 12.4, 12.4, H-6), 2.35 (1H, m, H-6), 1.73 (1H, m, H-7), 1.93 (1H, m, H-8), 2.02 (1H, m, H-8), 1.07 (3H, d, 6.5, H-10), 2.28 (1H, br d, 12.2, H-11), 3.28 (1H, dd, 12.4, 12.2, H-11), 3.82 (1H, m, H-12), 1.59 (1H, m, H-13), 1.82 (1H, m, H-13), 1.74 (1H, m, H-14), 1.78 (1H, m, H-14), 1.62 (1H, m, H-15), 2.17 (1H, m, H-15), 3.89 (1H, br d, 13.1, H-16), 1.56 (1H, m, H-17), 1.80 (1H, m, H-17), 1.99 (1H, m, H-18), 1.35 (1H, m, H-19), 1.97 (1H, m, H-19), 3.95 (1H, m, H-20), 0.96 (3H, d, 6.2, H-21), 1.39 (3H, d, 6.2, H-22), 2.90 (3H, s, H-23); ^{13}C NMR (CD_3OD) δ 57.0 (C-1), 24.6 (C-2), 27.3 (C-3), 128.5 (C-4), 66.6 (C-5), 35.7 (C-6), 28.9 (C-7), 39.4 (C-8), 135.4 (C-9), 21.6 (C-10), 33.8 (C-11), 55.9 (C-12), 19.5 (C-13), 18.3 (C-14), 24.5 (C-15, 55.4 (C-16), 38.1 (C-17), 25.0 (C-18, 42.0 (C-19), 53.4 (C-20), 21.7 (C-21), 18.0 (C-22), 41.3 (C-23).
15. Lycochinine A (**1**): colorless amorphous solid, $[\alpha]_D^{23}$ −15 (*c* 1.0, MeOH); IR (KBr) ν_{max} 3400, 2920, 1450, and 1130 cm^{-1}; ^{1}H and ^{13}C NMR (Table 1); ESIMS (pos.) *m*/*z* 428 (M+H)$^+$; HRESITOFMS *m*/*z* 428.3993 (M+H)$^+$, calcd for $C_{28}H_{50}N_3$ 428.4005.
16. Lycochinine B (**2**): colorless amorphous solid; $[\alpha]_D^{23}$ −5 (*c* 1.0, MeOH); IR (KBr) ν_{max} 3400, 2920, and 1450, and 1130 cm^{-1}; ^{1}H and ^{13}C NMR (Table 1); ESIMS (pos.) *m*/*z* 414 (M+H); HRESITOFMS *m*/*z* 414.3843 (M+H)$^+$, calcd for $C_{27}H_{48}N_3$ 414.3848.
17. Lycochinine C (**3**): colorless amorphous solid; $[\alpha]_D^{23}$ +62 (*c* 1.0, MeOH); IR (KBr) ν_{max} 3430, 2930, 2860, 1660, and 1440 cm^{-1}; ^{1}H and ^{13}C NMR (Table 1); ESIMS (pos.) *m*/*z* 444 (M+H)$^+$; HRESITOFMS *m*/*z* 444.3940 (M+H)$^+$, calcd for $C_{28}H_{50}N_3O$ 444.3948.