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Lyconesidines A–C, new alkaloids from *Lycopodium chinense*

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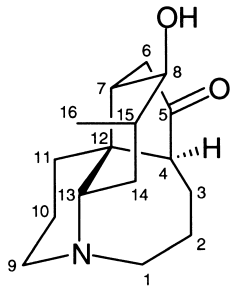
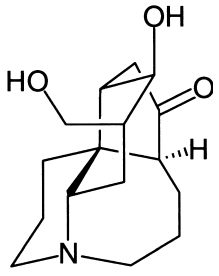
Abstract—Three new alkaloids, lyconesidines A (**1**), B (**2**), and C (**3**), have been isolated from the club moss *Lycopodium chinense*, and the structures and absolute stereochemistry were elucidated on the basis of 2D NMR data, X-ray analysis, and modified Mosher's method.

Many kinds of club moss (Lycopodiaceae) are known to be a rich source of *Lycopodium* alkaloids with unique heterocyclic frameworks of $C_{16}N$, $C_{16}N_2$, and $C_{27}N_3$ types.[1] Recently, we have reported the isolation of new alkaloids such as serratezomine A,[2] complanadine A,[3] lyconadin A,[4] and senepodine A[5] from *Lycopodium serratum* var. *serratum*,[2] *L. complanatum*,[3,4] and *L. chinense*,[5] respectively. Our continuing search for biogenetically interesting alkaloids from *L. chinense* led to the isolation of three new $C_{16}N$ alkaloids, lyconesidines A (**1**), B (**2**), and C (**3**). This paper describes the isolation and structure elucidation of **1**–**3**.



1



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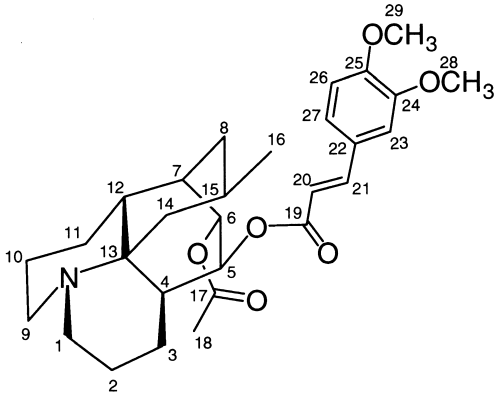

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The club moss *L. chinense* collected in Hokkaido was extracted with MeOH, and the MeOH extract was partitioned between AcOEt and 3% tartaric acid. Water-soluble materials, after being adjusted at pH 10 with sat. Na_2CO_3, were partitioned with $CHCl_3$. $CHCl_3$-soluble materials were subjected to an amino silica gel column (hexane/AcOEt, 1:0→0:1, and then $CHCl_3$/MeOH, 1:0→0:1), in which a fraction eluted with hexane/AcOEt (3:2) was purified by a silica gel column ($CHCl_3$/MeOH/AcOEt, 10:1:0.5) to afford lyconesidine A (**1**, 0.002% yield), and lyconesidine B (**2**, 0.005%) was obtained from the fraction eluted with $CHCl_3$/MeOH (9:1) and was crystallized from MeOH–H_2O. Lyconesidine C (**3**, 0.003%) together with a known $C_{16}N$ type alkaloid, lycodoline (**4**),[6] was yielded by C_{18} HPLC (25% CH_3CN/0.1% TFA) of the fraction eluted with hexane/AcOEt (4:1) in the amino silica gel column.

Lyconesidine A {**1**, $[\alpha]_D=-53°$ (*c* 1.0, MeOH)} was revealed to have the molecular formula, $C_{16}H_{25}NO_2$, by HRFABMS [*m*/*z* 264.1986 $(M+H)^+$, Δ +2.2 mmu]. IR absorptions implied the presence of a hydroxyl (3370 cm^{-1}) and carbonyl (1730 cm^{-1}) groups. ^1H and ^{13}C NMR data (Table 1) suggested the presence of one ketone, one sp^3 oxymethine, eight sp^3 methylenes, four sp^3 methines, one methyl, and one sp^3 quaternary carbon. Among them, one methine (δ_c 59.85) and two methylenes (δ_c 51.61 and 53.99) were ascribed to those bearing a nitrogen.

^1H–^1H COSY and HOHAHA experiments of **1** clearly revealed two structural units **a** (C-1–C-4) and **c** (C-9–C-11) shown in Fig. 1. The HMBC correlation for H_3-16

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Table 1. ^{1}H and ^{13}C NMR data of lyconesidine A (**1**) in CD_3OD at 300 K

	δ_H	δ_C	HMBC (^{1}H)
1a	2.89 (1H, brd, 15.1)	51.61	9a, 9b, 13
1b	3.23 (1H, m)		
2a	1.81 (1H, m)	31.03	
2b	1.87 (1H, m)		
3a	1.68 (1H, m)	27.05	1a, 4
3b	2.22 (1H, m)		
4	2.31 (1H, m)	57.68	7, 11a
5		219.94	4, 6a, 7
6a	2.43 (1H, d, 16.5)	41.76	
6b	2.74 (1H, dd, 16.5, 7.0)		
7	1.90 (1H, m)	44.64	
8	3.09 (1H, m)	74.46	6a, 7, 14a, 16
9a	3.11 (1H, m)	53.99	1b, 13
9b	3.21 (1H, m)		
10a	1.66 (1H, m)	23.38	
10b	2.01 (1H, m)		
11a	1.58 (1H, ddd, 13.3, 13.3, 3.7)	41.76	7, 9a, 13
11b	2.02 (1H, m)		
12		46.56	4, 6a, 7, 11b, 14a
13	3.12 (1H, m)	59.85	1a, 9a, 11b, 14a, 14b
14a	1.52 (1H, ddd, 13.3, 3.8, 3.8)	33.81	16
14b	2.28 (1H, m)		
15	2.20 (1H, m)	35.43	16
16	1.05 (3H, d, 7.1)	11.89	14b

of C-8 (δ_c 74.46) indicated the presence of the partial unit **b** (C-6–C-8 and C-13–C-16). Connections among these three units **a**–**c**, C-5 (δ_C 219.94), and C-12 (δ_C 46.56) were suggested by HMBC correlations as follows. HMBC correlations for H-4, H-7, H-11, and H-13 of C-12 gave rise to the connectivity of the three units through C-12. The connectivity between C-4 and C-6 through C-5 were elucidated by HMBC cross-peaks for H-4 (δ_H 2.31) and H-6a (δ_H 2.43) of C-5. Connectivities among C-1, C-9, and C-13 through N-1 were provided by HMBC correlations for H-1 to C-9 (δ_C 53.99) and C-13 (δ_C 59.85), H-9 to C-1 (δ_C 51.61) and C-13, and H-13 to C-1 and C-9. Thus, the gross structure of lyconesidine A was elucidated to be **1**.

The relative stereochemistry of **1** was deduced from cross-peaks observed in the phase sensitive NOESY spectrum as shown in computer-generated 3D drawing (Fig. 2). Chair conformations of a cyclohexane ring (C-7, C-8, and C-12–C-15) and a piperidine ring (N-1 and C-9–C-13) were suggested by NOESY correlations of H-9b to H-13 and H-11a, H-13 to H-11a and H_3-16, and H-7 to H-11a and H_3-16. NOESY correlations of H-4 to H-2a and H-10a indicated an α configuration of H-4. NOESY cross-peaks for H-3b to H-8 and H-14a suggested that H-3b, H-8, and H-14a were oriented to the same side. The absolute stereochemistry of lyconesidine A (**1**) was elucidated by applying a modified Mosher's method.[8] To determine the absolute configuration at C-8, **1** was converted into its (*S*)- and (*R*)-2-methoxy-2-trifluoromethylphenylacetic acid (MTPA) esters of the hydroxy group at C-8. The values of $\Delta\delta$ [δ(*S*-MTPA ester)$-\delta$(*R*-MTPA ester)] obtained from the ^{1}H NMR spectra of the MTPA esters suggested that the absolute configuration at C-8 was *S*.

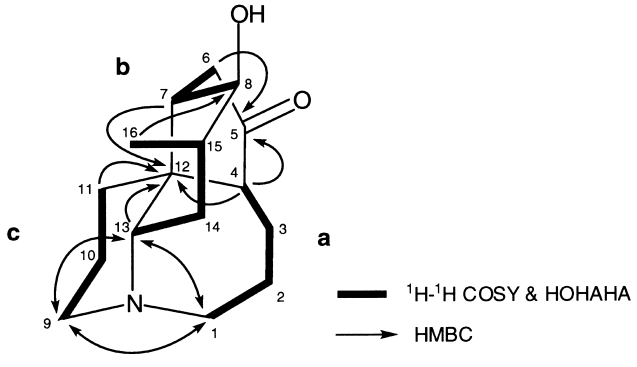


Figure 1. Selected 2D NMR correlations for lyconesidine A (**1**).

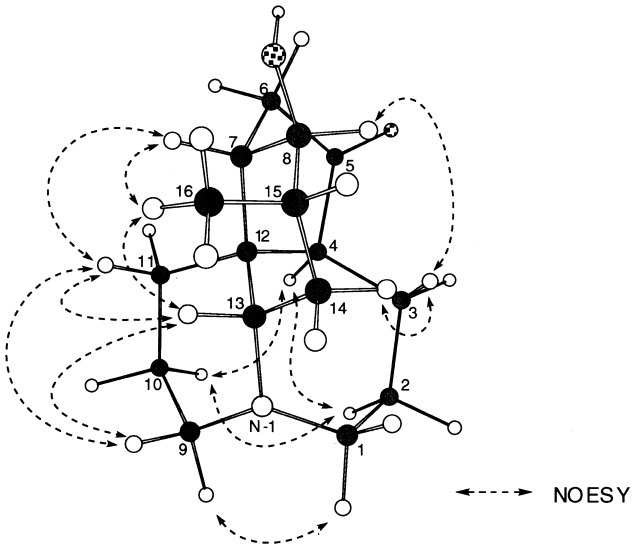


Figure 2. Selected NOESY correlations and relative stereochemistry for lyconesidine A (**1**).

Lyconesidine B {**2**, $[\alpha]_D=-71°$ (*c* 1.8, MeOH)} showed the pseudomolecular ion peak at *m/z* 280 $(M+H)^+$ and the molecular formula, $C_{16}H_{25}NO_3$, was established by HRFABMS [*m/z* 280.1898, $(M+H)^+$, Δ −1.5 mmu]. IR

Table 2. ^{1}H and ^{13}C NMR data of lyconesidine B (**2**) in CD_3OD at 300 K

	δ_H	δ_C	HMBC (^{1}H)
1a	2.81 (1H, brd, 15.4)	51.21	2, 3a, 3b, 9a, 9b, 13
1b	3.20 (1H, m)		
2	1.80 (2H, m)	31.80	1a, 3b, 4
3a	1.67 (1H, dd, 12.3, 12.3)	27.30	1a, 4
3b	2.20 (1H, m)		
4	2.29 (1H, dd, 12.4, 3.1)	57.91	2, 3a, 6a, 7, 11a
5		220.20	4, 6a, 6b, 7
6a	2.36 (1H, d, 18.1)	41.74	
6b	2.75 (1H, dd, 18.1, 7.2)		
7	1.86 (1H, d, 10.2)	46.10	6a, 11b
8	3.23 (1H, m)	73.84	6a, 7, 14a, 14b, 16a
9a	3.04 (1H, m)	54.20	1b, 10a, 11b
9b	3.14 (1H, ddd, 13.6, 13.6, 3.6)		
10a	1.59 (1H, m)	23.87	1a, 9a, 9b, 11a, 11b
10b	1.94 (1H, m)		
11a	1.57 (1H, ddd, 13.1, 13.1, 3.2)	42.69	4, 7, 13
11b	2.01 (1H, d, 13.1)		
12		46.59	3b, 4, 6a, 7, 10a, 11b, 14a
13	3.07 (1H, m)	59.65	1a, 9a, 11b, 14b
14a	1.77 (1H, m)	28.45	16a, 16b
14b	2.13 (1H, ddd, 13.5, 13.5, 4.6)		
15	2.17 (1H, m)	42.92	13, 14b, 16a
16a	3.71 (1H, dd, 10.9, 8.9)	60.47	8, 14b
16b	3.90 (1H, dd, 10.9, 5.8)		

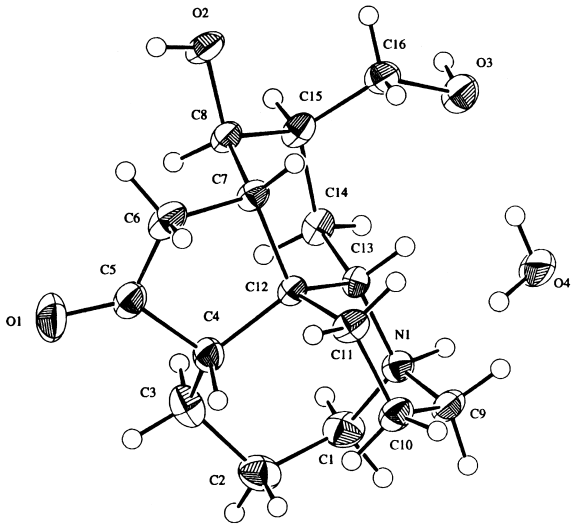


Figure 3. Molecular structure of lyconesidine B (**2**) containing one molecule of H_2O obtained by X-ray analysis (ORTEP drawing; ellipsoids are drawn at the 30% probability level).

absorptions implied the presence of hydroxyl (3430 cm^{-1}) and ketone (1730 cm^{-1}) functionalities. The ^1H and ^{13}C NMR (Table 2) spectra suggested that **2** had the same tetracyclic backbone framework as that of **1**, except for the presence of a hydroxy group at C-16 (δ_C 60.47, δ_H 3.71 and 3.90). The relative stereochemistry of lyconesidine B (**2**) was deduced by X-ray analysis (Fig. 3) of the crystal of **2** obtained from MeOH–H_2O.

Table 3. ^1H and ^{13}C NMR data of lyconesidine C (**3**) in CD_3OD at 300 K

	δ_H	δ_C	HMBC (^1H)
1a	3.00 (1H, dd, 4.8, 13.4)	48.45	
1b	3.77 (1H, ddd, 3.6, 13.4, 13.4)		
2a	1.81 (1H, m)	19.74	
2b	2.09 (1H, m)		
3a	1.58 (1H, m)	24.34	2b
3b	1.90 (1H, m)		
4	3.15 (1H, m)	30.86	2a, 5, 6, 14a
5	5.28 (1H, d, 7.1)	72.26	6, 7
6	4.77 (1H, brs)	76.83	5, 7, 8a
7	2.10 (1H, m)	41.56	5, 6
8a	1.40 (1H, ddd, 4.8, 13.3, 13.3)	39.55	6, 16
8b	1.93 (1H, m)		
9a	3.10 (1H, m)	48.59	11a
9b	3.90 (1H, m)		
10a	1.82 (1H, m)	24.90	
10b	2.02 (1H, m)		
11a	1.57 (1H, m)	21.22	9a
11b	2.16 (1H, m)		
12	1.83 (1H, m)	44.72	6, 8b
13		64.42	1a, 5, 7, 9a, 14a
14a	1.22 (1H, dd, 12.9, 12.9)	40.35	16
14b	2.90 (1H, dd, 6.0, 12.9)		
15	2.79 (1H, m)	25.75	7, 14a, 16
16a	1.08 (3H, d, 6.3)	23.66	
17		170.82	6, 18
18	2.09 (3H, s)	21.10	
19		167.31	5, 20, 21
20	6.40 (1H, d, 15.9)	115.51	21
21	7.64 (1H, d, 15.9)	147.62	23, 27
22		128.49	20, 21, 26
23	7.23 (1H, d, 2.0)	111.74	21, 27
24		150.89	26, 28
25		153.27	23, 27. 29
26	6.99 (1H, d, 8.3)	112.71	
27	7.19 (1H, dd, 2.0, 8.3)	124.41	21, 23
28	3.87 (3H, s)	56.47	
29	3.87 (3H, s)	56.59	

The absolute stereochemistry of lyconesidine B (**2**) was elucidated by applying a modified Mosher's method as followed.[8] The hydroxy group at C-16 of **2** was protected with triphenyl methyl (trityl) group and then esterified with its (*S*)- and (*R*)-MTPA chlorides, followed by hydrolysis of trityl ester with formic acid to give its (*S*)- and (*R*)-MTPA esters. The values of $\Delta\delta$ [δ(*S*-MTPA ester)$-\delta$(*R*-MTPA ester)] obtained from the ^1H NMR spectra of the MTPA esters suggested that the absolute configuration at C-8 was *S*.

HRFABMS data [*m/z* 498.2833, $(M+H)^+$, Δ −2.3 mmu] of lyconesidine C (**3**) revealed the molecular formula, $C_{29}H_{39}NO_6$. The ^1H and ^{13}C NMR (Table 3) spectra of **3** gave signals including six quaternary carbons (sp^2×5 and sp^3×1), eleven methines (sp^2×5 and sp^3×6), eight methylenes, and four methyls, suggesting that **3** had a similar backbone skeleton to that of lycodoline (**4**). In the ^{13}C NMR spectrum of **3**, signals due to the oxygen bearing carbons at δ_C 72.26 (d) and 76.83 (d), the nitrogen bearing carbons at δ_C 48.45 (t), 48.59 (t), and 64.42 (s), and two ester carbonyl carbon at δ_C 167.31 (s) and 170.82 (s) appeared. The structure of **3** was elucidated by 2D NMR (^1H–^1H COSY, HOHAHA, HMQC, and HMBC) data (Fig. 4). The ^1H–^1H COSY and HOHAHA spectra revealed connectivities as shown by the bold line (Fig. 4). This partial unit was connected to C-13 on the basis of HMBC correlations of H-1a, H-5, H-7, H-9a, and H-14a to C-13. The presence of an acetoxy at C-6 and a 3, 4-dimethoxy cinnamoyl ester at C-5 was revealed by HMBC correlations of H-6 and H_3-18 to C-17, and H-5 and H-20 to C-19.

The relative stereochemistry of **3** was deduced from NOESY correlations (Fig. 4). NOESY cross-peaks of H-6/H-8b, H-6/H-15, and H-5/H-3a suggested the stereochemistry at C-7 and C-15, an α-oriented acetoxy group at C-6, and an β-oriented 3, 4-dimethoxy cinnamoyl ester at C-5. The configurations at C-5 and C-6 were also supported by the small ^3J coupling (<1 Hz) between H-5 and H-6, both of which were oriented equatorially, and the two W-type couplings between H-5 and H-7, and between H-6 and H-12. NOESY correlations of H-4/H-9b and H-11b, and H-8a/H-12 implied the relative configurations at C-4, C-12, and C-13 together with a *cis*-fused quinolizidine ring. Thus the relative stereostructure of lyconesidine C was assigned as **3**.

A plausible biogenetic path of lyconesidines A (**1**), B (**2**), and C (**3**) was proposed as shown in Scheme 1 in which both **1** and **2** may be derived from lycodoline (**4**)[6] through an intermediate **A**. Compounds **1** and **2** are the first examples of fawcettidane-type alkaloids[7] without a hydroxy group or an olefin at C-13.

Lyconesidines A (**1**), B (**2**), and C (**3**) exhibited cytotoxicity against murine lymphoma L1210 cells with IC_{50} values of 18.0, 9.5, and 11.0 μg/ml, respectively. Furthermore, lyconesidines A (**1**) and B (**2**) inhibited the polymerization of tubulin[9] (IC_{50}, 300 and 250 μM, respectively).

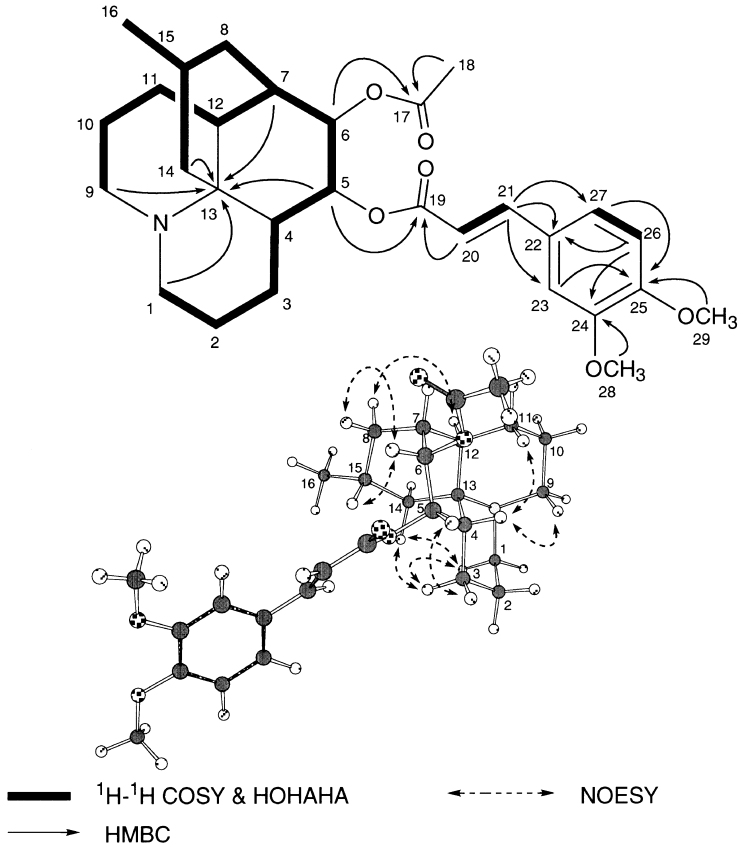
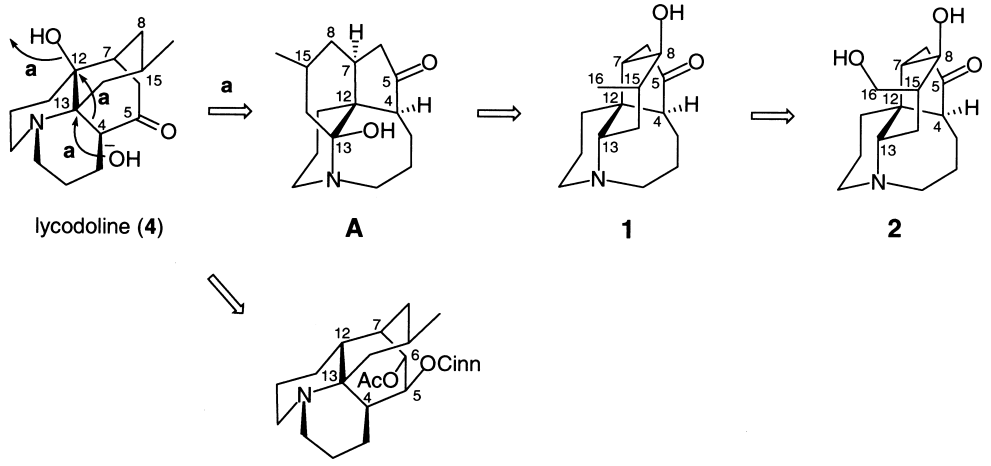


Figure 4. Selected 2D NMR correlations and relative configurations for lyconesidine C (**3**).



Scheme 1.

1. Experimental

1.1. General methods

^{1}H and 2D NMR spectra were recorded in CD_3OD and $CDCl_3$ on a 600 MHz spectrometer at 300 K. Chemical shifts were reported using residual CD_3OD (δ_H 3.31 and δ_C 49.00) and $CDCl_3$ (δ_H 7.26 and δ_C 77.03) as internal standards. Standard pulse sequences were employed for the 2D NMR experiments. HMBC spectra were recorded using a 50 ms delay time for long-range C–H coupling with *Z*-axis PFG. NOESY spectra were measured with a mixing time of 800 ms. FABMS was measured by using glycerol matrix.

1.2. Material

The club moss *Lycopodium chinense* was collected at

Kiyosato in Hokkaido in 2001. The botanical identification was made by Mr N. Yoshida, Health Sciences University of Hokkaido. A voucher specimen has been deposited in the herbarium of Hokkaido University.

1.3. Extraction and isolation

The club moss (2 kg) of *L. chinense* was extracted with MeOH (10 L×3). The MeOH extract (146 g) was partitioned between AcOEt and 3% tartaric acid. Water-soluble materials, after being adjusted at pH 10 with sat. Na_2CO_3, were partitioned with $CHCl_3$. $CHCl_3$ soluble materials (2.4 g) were subjected to an amino silica gel column (hexane/AcOEt, 1:0⟶0:1, and then $CHCl_3$/MeOH, 1:0⟶0:1). The fraction eluted with hexane/AcOEt (3:2) was separated by a silica gel column ($CHCl_3$/MeOH/AcOEt, 10:1:0.5) to afford lyconesidine A (**1**, 0.002%), and lyconesidine B (**2**, 0.005%) was crystallized [from MeOH–H_2O (1:1)] from the fraction eluted with $CHCl_3$/MeOH (9:1). Lyconesidine C (**3**, 0.003%) was purified by a C_{18} HPLC (40% CH_3CN/0.1% TFA) of the fraction eluted with hexane/AcOEt (4:1) together with a known $C_{16}N$ type alkaloid, lycodoline (**4**, 0.001%).[6]

1.3.1. Lyconesidine A (1). A colorless solid; $[\alpha]_D=-53°$ (*c* 1.0, MeOH); ^1H and ^{13}C NMR data (Table 1); FABMS *m/z* 264 $(M+H)^+$; HRFABMS *m/z* 264.1986 (M+H; calcd for $C_{16}H_{26}NO_2$, 264.1964); IR (neat) ν_{max} 3370, 2930, and 1730 cm^{-1}.

1.3.2. Lyconesidine B (2). Colorless needles; mp 170–171°C; $[\alpha]_D=-71°$ (*c* 1.8, MeOH); ^1H and ^{13}C NMR data (Table 2); FABMS *m/z* 280 $(M+H)^+$; HRFABMS *m/z* 280.1898 (M+H; calcd for $C_{16}H_{26}NO_3$, 280.1913); IR (KBr) ν_{max} 3430, 3316, 1730, 1455, and 1031 cm^{-1}.

1.3.3. Lyconesidine C (3). A colorless solid; $[\alpha]_D=-3°$ (*c* 1.0, MeOH); ^1H and ^{13}C NMR data (Table 3); FABMS *m/z* 498 $(M+H)^+$; HRFABMS *m/z* 498.2833 (M+H; calcd for $C_{29}H_{40}NO_6$, 498.2856); IR (neat) ν_{max} 2945, 1684, and 1040 cm^{-1}. UV (MeOH) λ_{max} 204 (ϵ 16400), 217 (14100), 236 (12100), 300 (sh, 13900), and 327 (18400).

1.3.4. (*R*)- and (*S*)-MTPA Ester of lyconesidine A (1). To a solution of **1** (0.2 mg) in CH_2Cl_2 (100 μl) were added (+)-MTPACl (0.8 μl), triethylamine (0.5 μl), and *N*,*N*-dimethylaminopyridine (40 μg). The mixture was allowed to stand at room temperature for 6 h. *N*,*N*-Dimethylamino-1,3-propandiamine (1.0 μl) was added, and after evaporation of solvent, the residue was applied to a silica gel column ($CHCl_3$–MeOH, 10:1) to give the (*S*)-MTPA ester of **1** (0.3 mg, 82%). The (*R*)-MTPA ester of **1** was prepared according to the same procedure as described above.

(*R*)-MTPA ester of **1**: ^1H NMR ($CDCl_3$) δ 3.25 and 3.47 (m, H-1), 1.88 and 2.20 (m, H-2), 1.71 and 2.44 (m, H-3), 2.16 (m, H-4), 1.97 and 2.55 (m, H-6), 2.23 (m, H-7), 4.50 (m, H-8), 3.24 and 3.65 (m, H-9), 1.58 and 2.03 (m, H-10), 1.82 and 2.00 (m, H-11), 3.60 (m, H-13), 2.11 and 2.34 (m, H-14), 2.44 (m, H-15), 1.03 (d, 6.8, H-16). FABMS *m/z* 480 $(M+H)^+$; HRFABMS *m/z* 480.2344 (M+H; calcd for $C_{26}H_{33}NO_4F_3$, 480.2362).

(*S*)-MTPA ester of **1**: ^1H NMR ($CDCl_3$) δ 3.26 and 3.47 (m, H-1), 1.88 and 2.19 (m, H-2), 1.72 and 2.44 (m, H-3), 2.19 (m, H-4), 2.14 and 2.66 (m, H-6), 2.29 (m, H-7), 4.50 (m, H-8), 3.25 and 3.66 (m, H-9), 1.58 and 2.03 (m, H-10), 1.87 and 2.02 (m, H-11), 3.60 (m, H-13), 2.10 and 2.34 (m, H-14), 2.44 (m, H-15), 0.89 (d, 6.7, H-16). FABMS *m/z* 480 $(M+H)^+$; HRFABMS *m/z* 480.2358 (M+H; calcd for $C_{26}H_{33}NO_4F_3$, 480.2362).

1.3.5. (*R*)- and (*S*)-MTPA Ester of lyconesidine B (2). To a solution of **2** (0.75 mg) in CH_2Cl_2 (200 μl) were added trityl chloride (2.4 mg), triethylamine (3.7 μl), and *N*,*N*-dimethylaminopyridine (150 μg). The mixture was allowed to stand at room temperature for 3 h. After evaporation of solvent, the residue was applied to a silica gel column ($CHCl_3$–MeOH, 8:1) to give the trityl ester of **2**, to which were added (+)-MTPACl (1.5 μl), triethylamine (3.7 μl), and *N*,*N*-dimethylaminopyridine (150 μg) in CH_2Cl_2 (200 μl). The mixture was allowed to stand at room temperature for 3 h. After evaporation of solvent, the residue was applied to a silica gel column ($CHCl_3$) to give the (*S*)-MTPA ester of trityl ester of **2**, which was hydrolyzed with formic acid to give the (*S*)-MTPA ester of **2**. The (*R*)-MTPA ester of **2** was prepared according to the same procedure as described above.

(*R*)-MTPA ester of **2**: ^1H NMR ($CDCl_3$) δ 1.93 (d, 17.2, H-6), 2.51 (dd, 17.2, 6.8, H-6), 2.31 (dd, 10.1, 7.6, H-7), 4.64 (dd, 10.1, 4.5, H-8), 3.99 (dd, 13.6, 4.1, H-13), 2.03 (m, H-14), 2.55 (m, H-14), 2.50 (m, H-15), 3.58 (dd, 11.8, 4.8, H-16), 3.87 (dd, 11.8, 9.7, H-16). FABMS *m/z* 496 $(M+H)^+$; HRFABMS *m/z* 496.2309 (M+H; calcd for $C_{26}H_{33}NO_5F_3$, 496.2311).

(*S*)-MTPA ester of **2**: ^1H NMR ($CDCl_3$) δ 2.12 (d, 17.1, H-6), 2.65 (dd, 17.1, 7.3, H-6), 2.34 (m, H-7), 4.65 (dd, 10.4, 4.7, H-8), 3.89 (dd, 13.5, 4.3, H-13), 2.02 (m, H-14), 2.36 (m, H-14), 2.43 (m, H-15), 3.39 (dd, 12.1, 4.9, H-16), 3.71 (dd, 12.1, 9.3, H-16). FABMS *m/z* 496 $(M+H)^+$; HRFABMS *m/z* 496.2307 (M+H; calcd for $C_{26}H_{33}NO_5F_3$, 496.2311).

1.4. Crystal data of lyconesidine B (2)

Lyconesidine B (**2**) was crystallized from MeOH–H_2O to give colorless needles (mp. 170–171°C). Crystal data: $C_{16}H_{26}NO_3 \cdot H_2O$, Mr=298.40, crystal dimensions 0.20×0.10×0.10 mm^3, tetragonal, space group $P2_12_12_1$ (no. 19), *a*=8.89(6), *b*=20.04(7), *c*=8.16(8) Å, V=1452(16) $Å^3$, *Z*=4, D_{calc}=1.364 g/cm^3. All measurements were made on a Rigaku AFC7R diffractometer with graphite monochromated Mo Kα radiation (λ=0.71069 Å) and a 18 kW rotating anode generator. The data were collected at 23±1°C by using the $\omega-2\theta$ scan technique to a maximum 2θ value of 55.5°. A total of 1990 reflections were collected. The intensities of three representative reflections were measured after every 150 reflections. No decay correction was applied. The linear absorption coefficient, μ, for Mo Kα radiation was 1.0 cm^{-1}. Azimuthal scans of several reflections indicated no need for an absorption correction. The data were corrected for the Lorentz and polarization effects. A correction for secondary extinction was applied (coefficient=7.82080×10^{-7}).The structure was solved by

SIR92 and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The final cycle of full-matrix least-squares refinement was based on 1969 observed reflections ($I > -10.00\sigma(I)$) and 191 variable parameters and converged with unweighted and weighted agreement factors of R=0.059, R_w=0.115. All calculations were performed using the teXsan crystallographic software package of Molecular Structure Corporation. The refined fractional atomic coordinates, bond lengths, bond angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

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