Himeradine A, a Novel C₂₇N₃ Type Alkaloid from *Lycopodium chinense*

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Supporting Information

Experimental Section

Figure S1. ¹H NMR spectrum of himeradine A (**1**) in CD₃OD.

Figure S2. ¹³C NMR spectrum of himeradine A (**1**) in CD₃OD.

Figure S3. ¹H-¹H COSY spectrum of himeradine A (**1**) in CD₃OD.

Figure S4. HOHAHA spectrum of himeradine A (**1**) in CD₃OD.

Figure S5. NOESY spectrum of himeradine A (**1**) in CD₃OD.

Figure S6. HMQC spectrum of himeradine A (**1**) in CD₃OD.

Figure S7. HMBC spectrum of himeradine A (**1**) in CD₃OD.

Experimental Section

General Procedures. ^1H and 2D NMR spectra were recorded on a 600 MHz spectrometer at 300K, while ^{13}C NMR spectra were measured on a 150 MHz spectrometer. The NMR sample of himeradine A (**1**) was prepared by dissolving 1.0 mg in 30 μL of CD_3OD or pyridine- d_5 in 2.5 mm micro cells (Shigemi Co. Ltd.) and chemical shifts were reported using residual CD_3OD (δ_{H} 3.31 and δ_{C} 49.0) or pyridine- d_5 (δ_{H} 7.21 and δ_{C} 135.5) as internal standards. Standard pulse sequences were employed for the 2D NMR experiments. ^1H - ^1H COSY, HOHAHA, and NOESY spectra were measured with spectral widths of both dimensions of 4800 Hz, and 32 scans with two dummy scans were accumulated into 1K data points for each of 256 t_1 increments. NOESY and HOHAHA spectra in the phase sensitive mode were measured with a mixing time of 800 and 30 ms, respectively. For HMQC spectra in the phase sensitive mode and HMBC spectra, a total of 256 increments of 1K data points were collected. For HMBC spectra with Z-axis PFG, a 50 ms delay time was used for long-range C-H coupling. Zero-filling to 1K for F_1 and multiplication with squared cosine-bell windows shifted in both dimensions were performed prior to 2D Fourier transformation. FABMS was measured by using glycerol as a matrix.

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.

Isolation. The club moss *L. chinense* (2 kg) was extracted with MeOH (10 L $\times$ 3). The MeOH extract (146 g) was partitioned between EtOAc 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/EtOAc, 1:0 $\rightarrow$ 0:1). The fraction eluted with hexane/EtOAc (3:2) was separated by a silica gel column ($\text{CHCl}_3/\text{MeOH}/\text{EtOAc}$, 10:1:0.5) and then C_{18} HPLC (Phenomenex LUNA C_{18} (2), 5 μm , Shimadzu, 10 $\times$ 250 mm; eluent, 26% $\text{CH}_3\text{CN}/0.1\%$ TFA; flow rate, 2 mL/min; UV detection at 220 nm) to afford himeradine A (**1**, 0.001%), lucidine B (**2**, 0.001%), lyconesidines A⁹ (0.002%), B⁹ (0.005%), and C⁹ (0.003%), lycodoline¹¹ (0.001%), and senepodine A⁸ (0.003%).

Himeradine A (1): colorless solid; $[\alpha]_{\text{D}}^{25}$ -23° (c 0.3, MeOH); IR (neat) ν_{max} 3411, 2928, 1640, and 1398 cm^{-1} ; ^1H and ^{13}C NMR data (Table 1); FABMS m/z 452 ($\text{M}+\text{H}$)⁺; HRFABMS m/z 452.3647 ($\text{M}+\text{H}$; calcd for $\text{C}_{29}\text{H}_{46}\text{N}_3\text{O}$, 452.3641).

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Figure S2. ^{13}C NMR spectrum of himeradine A (1) in CD_3OD .

Figure S3. ^1H - ^1H COSY spectrum of himeradine A (1) in CD_3OD .

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