SUPPLEMENTARY MATERIAL

A New Lycopodine-type Alkaloid from *Lycopodium japonicum*

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A new lycopodine-type alkaloid, 12β-hydroxy-acetylfawcettiine N-oxide (1), together with seven known analogues, acetyllycoposerramine M (2), lycopodine (3), lycoclavine (4), diphaldine A (5), lycoposerramine K (6), 11β-hydroxy-12-epilycodoline (7) and fawcettiine (8), were isolated from *Lycopodium japonicum*. Their structures were established by mass spectrometry and 1D and 2D NMR techniques. The isolated alkaloids were assayed for their inhibition activities against acetylcholinesterase, but no inhibitory activities for the compounds were detected.

**Keywords:** *Lycopodium japonicum*; Lycopodiaceae; lycopodine-type alkaloids

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Supporting information

Spectroscopic data of the known compounds 2-8.

Figure 2. Selected 2D NMR correlations of 1.

Original spectra of compound 1.

- ESI-MS
- HR-ESI-MS
- IR Spectrum
- UV Spectrum
- $^1$H NMR Spectrum (500 MHz, CDCl$_3$)
- $^{13}$C NMR Spectrum (125 MHz, CDCl$_3$)
- $^1$H-$^1$H COSY Spectrum
- HSQC Spectrum
- HMBC Spectrum
- ROESY Spectrum
Spectroscopic data of the known compounds 2-8.

**acetyllycoposerramine M (2)**
Colorless solid; C\textsubscript{18}H\textsubscript{27}NO\textsubscript{3}; MW: 305; \textsuperscript{1}H-NMR (500 MHz, CDCl\textsubscript{3}) $\delta$H: 5.12 (m, H-11), 3.26 (m, H-1a), 3.24 (m, H-4), 0.77 (d, $J$ = 6.5 Hz, H-16); \textsuperscript{13}C-NMR (125 MHz, CDCl\textsubscript{3}) $\delta$C: 214.0 (s, C-5), 169.9 (s, C-17), 72.1 (d, C-11), 58.7 (s, C-13), 46.9 (t, C-1), 46.5 (d, C-12), 45.2 (d, C-4), 44.2 (t, C-6), 44.1 (t, C-8), 43.6 (t, C-14), 41.9 (t, C-9), 34.9 (d, C-7), 30.8 (t, C-10), 25.2 (d, C-15), 22.6 (q, C-16), 21.7 (q, C-17), 19.8 (t, C-3), 19.1 (t, C-2).

**lycopodine (3)**
Colorless solid; C\textsubscript{16}H\textsubscript{25}NO; MW: 247; \textsuperscript{1}H-NMR (500 MHz, CDCl\textsubscript{3}) $\delta$H: 3.30 (td, 14.0, 3.5, H-9a), 3.07 (td, 12.0, 3.0, H-1a), 2.78 (d, 12.0, H-1b), 0.75 (d, 6.5, H-16); \textsuperscript{13}C-NMR (125 MHz, CDCl\textsubscript{3}) $\delta$C: 213.0 (s, C-5), 60.0 (s, C-13), 47.1 (t, C-9), 46.5 (t, C-1), 44.7 (d, C-12), 42.9 (t, C-6), 42.8(d, C-4), 42.7 (t, C-14), 42.3 (t, C-8), 36.6 (d, C-7), 25.8 (t, C-10), 25.2 (d, C-15), 24.9 (t, C-11), 22.7 (q, C-16), 19.3 (t, C-3), 18.6 (t, C-2).

**lycoclavine (4)**
Colorless solid; C\textsubscript{18}H\textsubscript{29}NO\textsubscript{3}; MW: 307; \textsuperscript{1}H-NMR (500 MHz, CDCl\textsubscript{3}) $\delta$H: 4.69 (s, H-5), 2.07 (s, H-18), 0.91 (d, 6.5, H-16); \textsuperscript{13}C-NMR (125 MHz, CDCl\textsubscript{3}) $\delta$C: 170.2 (s, C-17), 80.0 (d, C-5), 71.6 (d, C-6), 57.8 (s, C-13), 46.7 (t, C-1), 46.6 (t, C-9), 43.5 (d, C-12), 41.0 (d, C-7), 40.1 (t, C-14), 39.6 (t, C-8), 30.0 (d, C-4), 25.2 (t, C-10), 25.0 (t, C-11), 24.0 (d, C-15), 23.5 (q, C-16), 22.0 (t, C-3), 21.4 (q, C-18), 19.8 (t, C-2).

**diphaladine A (5)**
Colorless oil; C\textsubscript{16}H\textsubscript{25}NO\textsubscript{4}; MW: 295; \textsuperscript{1}H-NMR (500 MHz, CDCl\textsubscript{3}) $\delta$H: 4.40 (dt, 12.0, 2.0, H-9a), 4.08 (s, H-11a), 3.90 (d, 10.0, H-4), 0.89 (d, 6.5, H-16). \textsuperscript{13}C-NMR (125 MHz, CDCl\textsubscript{3}) $\delta$C: 209.7 (s, C-5), 73.4 (s, C-13), 72.4 (s, C-12), 72.0 (s, C-11), 63.2 (t,
C-1), 55.7 (t, C-9), 48.6 (d, C-4), 45.1 (t, C-6), 40.4 (d, C-7), 36.9 (t, C-8), 30.2 (t, C-14), 26.5 (t, C-10), 24.7 (d, C-15), 22.4 (q, C-16), 21.5 (t, C-2), 17.5 (t, C-3).

**lycoposerramine K (6)**

Colorless solid; C_{16}H_{23}NO_2; MW: 261; ^1H-NMR (500 MHz, CDCl_3) δ_H: 5.73 (s, H-11), 3.85 (d, 2.5, H-6), 0.86 (d, 6.0, H-16); ^13C-NMR (125 MHz, CDCl_3) δ_C: 210.9 (s, C-5), 139.2 (s, C-12), 120.9 (d, C-11), 78.1 (d, C-6), 59.8 (s, C-13), 49.5 (d, C-4), 47.9 (d, C-7), 47.7 (t, C-1), 45.0 (t, C-9), 39.1 (t, C-8), 36.9 (t, C-14), 26.3 (t, C-10), 25.5 (d, C-15), 22.7 (t, C-2), 22.7 (q, C-16), 19.3 (t, C-3).

**11β-hydroxy-12-epilycodoline (7)**

Colorless solid; C_{16}H_{26}NO_3; MW: 280; ^1H-NMR (500 MHz, CDCl_3) δ_H: 2.86 (t, 12.5, H-4), 0.82 (d, 6.0, H-16). ^13C-NMR (125 MHz, CDCl_3) δ_C: 212.2 (s, C-5), 73.6 (d, C-11), 70.7 (s, C-12), 62.1 (s, C-13), 53.4 (d, C-4), 48.3 (t, C-1), 45.6 (t, C-6), 43.4 (t, C-9), 40.5 (d, C-7), 37.3 (t, C-8), 31.4 (t, C-10), 25.0 (t, C-14), 24.6 (t, C-2), 23.8 (d, C-15), 22.2 (q, C-16), 17.9 (t, C-3).

**fawcettiine (8)**

Colorless solid; C_{18}H_{29}NO_3; MW: 307; ^1H-NMR (500 MHz, CDCl_3) δ_H: 5.11 (s, H-5), 3.21 (t, 12, H-8), 1.43 (m, H-18), 1.08 (d, 6.5, H-16). ^13C-NMR (125 MHz, CDCl_3) δ_C: 170.4 (s, C-17), 78.7 (d, C-8), 69.5 (d, C-5), 55.0 (s, C-13), 47.4 (t, C-1), 46.7 (t, C-9), 43.2 (d, C-12), 41.3 (d, C-7), 41.0 (t, C-14), 31.9 (d, C-15), 31.2 (d, C-4), 25.9 (t, C-10), 24.3 (t, C-6), 24.2 (t, C-11), 22.6 (t, C-3), 21.5 (q, C-18), 20.8 (q, C-16), 19.8 (t, C-2).
Figure 2. Selected 2D NMR correlations of 1.
Original spectra of compound 1.

ESI-MS:
Original spectra of compound 1.

HR-ESI-MS:

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IR Spectrum

Sample : NYQ-1  Frequency Range : 399.246 - 3996.32  Measured on : 21/09/2015
Technique : KBr  压片  
Customer : 150921IR0  Resolution : 4
Zerofilling : 2
Instrument : Tensor27  Acquisition : Double Sided, Forward
Sample Scans : 16

Transmittance [%]

Wavenumber cm⁻¹
UV Spectrum

File Name: NYQ-1
Created: 15:34 15-09-16
Mode: Abs.
Scan Speed: Medium
Scan Time: 5.0
Step Interval: 0.2

Wavelength (nm) | Abs
---|---
203.60 | 0.1054
270.40 | 0.0148
$^1$H NMR:
HSQC:
