SUPPLEMENTARY MATERIAL

Two New Lycopodium Alkaloids from *Phlegmariurus phlegmaria* (L.)

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Two new Lycopodium alkaloids, 4 β -hydroxynankakurine B (**1**) and $\Delta^{13,N}$, N_{α} -methylphlegmarine- N_{β} -oxide (**2**), together with three known analogues, lycoposerramine E (**3**), nankakurine B (**4**) and lobscurinol (**5**), were isolated from *Phlegmariurus phlegmaria*. Their structures were established by mass spectrometry and 1D and 2D NMR techniques.

Keywords: *Phlegmariurus phlegmaria*; Huperziaceae; Lycopodium alkaloids

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Supporting information

Spectroscopic data of the known compounds **3-5**.

Figure S1. Selected 2D NMR correlations of **1**.

Original spectra of compound **1**.

ESI-MS

HR-ESI-MS

IR Spectrum

UV Spectrum

^1H NMR Spectrum (500 MHz, CDCl_3)

^{13}C NMR Spectrum (125 MHz, CDCl_3)

COSY Spectrum

HSQC Spectrum

HMBC Spectrum

ROESY Spectrum

Figure S2. Selected 2D NMR correlations of **2**.

Original spectra of compound **2**.

ESI-MS

HR-ESI-MS

IR Spectrum

UV Spectrum

^1H NMR Spectrum (500 MHz, CDCl_3)

^{13}C NMR Spectrum (125 MHz, CDCl_3)

COSY Spectrum

HSQC Spectrum

HMBC Spectrum

ROESY Spectrum

Spectroscopic data of the known compounds **3-5**.

lycposerramines-E (3)

Colorless solid, C₁₆H₂₃NO₃, MW: 277; ¹H-NMR (CDCl₃, 500 MHz): δ 4.14 (1H, td, *J* =15.0, 3.0 Hz, H-9a), 4.02 (1H, td, *J* =9.0, 3.0 Hz, H-1a), 3.26 (1H, d, *J* =2.5 Hz, H-6a), 3.19 (1H, d, *J* =17.0 Hz, H-9b), 1.12 (3H, d, *J* =7.0 Hz, H-16); ¹³C-NMR (CDCl₃, 125 MHz): δ 219.0 (s, C-5), 172.7 (s, C-13), 138.7 (s, C-12), 135.3 (s, C-7), 82.2 (s, C-4), 50.8 (t, C-9), 49.9 (t, C-1), 44.5 (t, C-6), 40.3 (t, C-3), 39.9 (t, C-14), 38.2 (t, C-8), 28.3 (d, C-15), 23.8 (t, C-10), 23.6 (t, C-11), 23.4 (q, C-16), 20.5 (t, C-2).

nankakurine B (4)

Colorless gum, C₁₈H₃₂N₂, MW: 276; ¹H-NMR (CDCl₃, 500 MHz): δ 4.14 (1H, td, *J* =15.0, 3.0 Hz, H-9a), 4.02 (1H, td, *J* =9.0, 3.0 Hz, H-1a), 3.26 (1H, d, *J* =2.5 Hz, H-6a), 3.19 (1H, d, *J* =17.0 Hz, H-9b), 1.12 (3H, d, *J* =7.0 Hz, H-16); ¹³C-NMR (CDCl₃, 125 MHz): δ 63.5 (d, C-13), 57.8 (s, C-5), 57.3 (t, C-9), 48.6 (t, C-1), 43.4 (q, C-17), 41.1 (t, C-8), 39.2 (t, C-14), 38.0 (t, C-6), 35.6 (d, C-12), 35.2 (q, C-18), 34.2 (d, C-10), 33.0 (d, C-7), 31.4 (t, C-11), 24.7 (t, C-4), 22.7 (q, C-16), 20.9 (d, C-15), 20.0 (t, C-3), 18.4 (t, C-2).

lobscurinol (5)

Colorless gum, C₁₇H₂₅NO₂, MW: 275; ¹H-NMR (C₅D₅N, 500 MHz): δ 6.13 (1H, dd, *J* =11.0, 7.0 Hz, H-3), 5.92 (1H, s, H-15), 4.60 (1H, d, *J* = 5.0 Hz, H-5), 3.71 (1H, ddd, *J* = 25.5, 11.5, 2.0 Hz, H-2a), 3.45 (1H, td, *J* =15.0, 3.0 Hz, H-9a), 3.17 (1H, m, H-9a), 2.86 (1H, td, *J* =13.5, 3.0 Hz, H-11a), 2.29 (3H, s, N-CH₃), 1.73 (3H, s, H-16); ¹³C-NMR (C₅D₅N, 125 MHz): δ 199.9 (s, C-13), 156.9 (s, C-15), 147.5 (s, C-4), 131.1 (d, C-3), 124.7 (d, C-14), 73.7 (d, C-5), 58.2 (s, C-12), 56.2 (t, C-9), 54.7 (t, C-1), 47.6 (q, C-17), 38.3 (d, C-7), 38.1 (t, C-6), 31.0 (t, C-8), 29.8 (t, C-11), 29.2 (t, C-2), 25.6 (t, C-10), 23.7 (q, C-16).

Figure S1. Selected 2D NMR correlations of **1**.

Original spectra of compound **1**.

ESI-MS:

Nmws5 11 (0.211) Cm (11-1:5x10.000)

1: MS2 ES+
3.69e7

Original spectra of compound 1.

HR-ESI-MS:

Qualitative Analysis Report

Data Filename	Nmws-5.d	Sample Name	Nmws-5
Sample Type	Sample	Position	P1-D1
Instrument Name	Instrument 1	User Name	
Acq Method	SIBU.m	Acquired Time	12/29/2014 10:33:41 AM
IRM Calibration Status	Success	DA Method	Default.m
Comment			

Sample Group		Info.
Acquisition SW	6200 series TOF/6500 series	
Version	Q-TOF B.05.01 (B5125.2)	

User Spectra

Peak List

m/z	z	Abund
208.1696	1	27282.72
307.238	1	59135.76
308.2421	1	16459.8
321.2537	1	23985.77
323.2329	1	14043.93

Formula Calculator Element Limits

Element	Min	Max
C	3	30
H	0	60
O	0	5
N	0	5

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C18 H32 N2 O	292.2515	293.2587	293.2596	-0.9	-3.0	4.0000

--- End Of Report ---

IR Spectrum

Sample : Nmws-5		Frequency Range : 399.246 - 3996.32		Measured on : 19/12/2014	
Technique : KBr压片	Resolution : 4	Instrument : Tensor27		Sample Scans : 16	
Customer : 141219IR0	Zerofilling : 2	Acquisition : Double Sided,Forw			

UV:

¹H NMR:

Current Data Parameters
NAME MWS-5
EXPNO 10
PROCNO 1
F2 - Acquisition Parameters
Date_ Time 20140523 14.22
INSTRUM spect
PROBHD 5 mm 1ABBO BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 20.91
DW 48.400 usec
DE 6.50 usec
TE 298.3 K
D1 1.00000000 sec
NUC1 1H
P1 12.56 usec
PLW1 16.0000000 W
SFO1 500.1330885 MHz
F2 - Processing parameters
SI 65536
SF 500.1300000 MHz
WDW LM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

¹³C NMR:

Current Data Parameters
NAME: 1005-5
EXPNO: 11
PROCNO: 1
F2 - Acquisition Parameters
Date_ : 20140523
Time: 14.55
INSTRUM: spect
PROBHD: 5mm PABBO BH-
1H1HPRG4
TD: 65536
SOLVENT: CDCl3
DS: 4
SWH: 29761.864 Hz
FIDRES: 0.344111 Hz
AQ: 1.101084 sec
RG: 197.02
AQ: 6.580 sec
RG: 6.580 sec
TE: 298.4 K
D1: 0.000000 sec
d11: 0.000000 sec
DELTA: 1.8999998 sec
NUC1: ¹³C
PLW1: 53.7029911 W
PLW2: 25.770357 MHz
NUC2: ¹H
CPOBPG2: 3000 sec
PLW2: 15.6900025 W
PLW12: 0.3425000 W
PLW13: 0.2233995 W
SFO2: 500.136065 MHz
F2 - Processing parameters
SI: 32768
WDW: EM
SSB: 0
LB: 1.00 Hz
GB: 0
PC: 1.40

H-H COSY:

HSQC:

HMBC:

ROESY:

Figure S2. Selected 2D NMR correlations of **2**.

Original spectra of compound **2**.

ESI-MS:

Nmws10 32 (0.645) Cm (31:35-2:5x10.000)

1: MS2 ES+
5.33e7

HR-ESI-MS:

Qualitative Analysis Report

Data Filename	Nmws-10.d	Sample Name	Nmws-10
Sample Type	Sample	Position	P1-F4
Instrument Name	Instrument 1	User Name	
Acq Method	SIBU.m	Acquired Time	12/29/2014 2:12:27 PM
IRM Calibration Status	Success	DA Method	Default.m
Comment			
Sample Group	Info.		
Acquisition SW	6200 series TOF/6500 series		
Version	Q-TOF B.05.01 (B5125.2)		

User Spectra

Peak List

m/z	z	Abund	Formula	Ion
121.0509	1	133856.58		
279.2435	1	705739.5	C17 H30 N2 O	(M+H)+
280.2466	1	122375.13	C17 H30 N2 O	(M+H)+
295.238	1	32517.05		
922.0098	1	51590.7		

Formula Calculator Element Limits

Element	Min	Max
C	0	50
H	0	120
O	0	10
N	0	3

Formula Calculator Results

Formula	CalculatedMass	CalculatedMz	Mz	Diff. (mDa)	Diff. (ppm)	DBE
C17 H30 N2 O	278.2358	279.2431	279.2435	-0.4	-1.3	4.0000

--- End Of Report ---

IR Spectrum:

Sample : Nmws-10		Frequency Range : 399.246 - 3996.32		Measured on : 19/12/2014	
Technique : KBr压片	Resolution : 4	Instrument : Tensor27		Sample Scans : 16	
Customer : 141219IR1	Zerofilling : 2	Acquisition : Double Sided,Forw			

UV:

¹H NMR:

Current Data Parameters
NAME MWS-10
EXPNO 1
PROCNO 1
F2 - Acquisition Parameters
Date_ 20141003
Time 20.01
INSTRUM spect
PROBHD 5 mm 1ABBO BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10330.578 Hz
FIDRES 0.157632 Hz
AQ 3.1719923 sec
RG 71.83
DW 48.400 usec
DE 6.50 usec
TE 300.9 K
D1 1.00000000 sec
NUC1 1H
P1 12.81 usec
PLW1 16.00000000 W
SFO1 500.1340885 MHz
F2 - Processing parameters
SI 32768
SF 500.1340885 MHz
WDW LM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

¹³C NMR:

Current Data Parameters
NAME: MWS-10
PROCNO: 1
F2 - Acquisition Parameters
Date_: 20141003
Time: 20.04
INSTRUM: spect
PROBHD: 5 mm PABBO BH-
PULPROG: zgpg30
F1: 125.76037 MHz
SOLVENT: CDCl3
NS: 1024
DS: 4
SWH: 20791.964 Hz
FIDRES: 0.454131 Hz
AQ: 1.100548 sec
RG: 327.66
DWT: 16.800 usec
DE: 7.50 usec
TE: 300.2 K
D1: 2.00000000 sec
d11: 0.05000000 sec
DELTA: 1.89999998 sec
NUC1: 13C
P1: 13.98 usec
PL1: 0.00 dB
SFO1: 125.76037 MHz
CPCPRG2: waltz16
NUC2: 1H
PCPD2: 8000 usec
PLW2: 15.99000020 W
PLW12: 0.41014001 W
PLW13: 0.41014001 W
SFO2: 500.1350005 MHz
F2 - Processing parameters
SI: 327.66
SF: 125.7577890 MHz
WDW: EM
SSB: 0
LB: 0.100 Hz
GB: 0
PC: 1.40

COSY:

[illegible]

HSQC:

1H NMR Spectrum (400 MHz, CDCl₃)

Chemical Shifts (ppm): 9.8, 7.5, 6.5, 5.5, 4.5, 3.5, 2.5, 1.5, 0.5

Integration: 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00, 1.00

Peak Data:

Chemical Shift (ppm)	Integration
9.8	1.00
7.5	1.00
6.5	1.00
5.5	1.00
4.5	1.00
3.5	1.00
2.5	1.00
1.5	1.00
0.5	1.00

ROESY:

Current: Data Parameters	
NAME	WFS-10
EXPNO	9
PROCNO	1
Data - Acquisition Parameters	
Date_	20100905
Time	3:16
INSTRUM	spect
5 mm F4000 J8-	
PROBHD	5mmF4000J8
TD	2048
TD0PROC	128
SOLVENT	CDCl3
NS	9
DS	4
SWH	2512.32 Hz
F2	500.13609 MHz
F1F2	500.13609 MHz
RG	6.4076020 sec
RG2	28.24
DW	199.300 tsec
DE	5.79 tsec
TE	300.2 K
D1	0.000000000000000000 sec
D11	1.793151900 sec
d12	0.020000000 sec
d122	0.000000000 sec
D13	300.000000000000000000 sec
D14	1.000 sec
T15	200.000 tsec
SILNCR	123
double	250.000000000000000000 sec
flip	1
flip1	1
flip2	1
NUC1	13
P1	12.01 tsec
P2	250.0 tsec
P3	250.0 tsec
P4	250.0 tsec
PW1	16.000000000000000000 sec
PW10	3.788489993 tsec
PW12	1.000100000 sec
ST01	500.1303495 MHz
T1 - Acquisition parameters	
TD	256
F2	500.13609 MHz
F1F2	9.914698 Lx
SW	5.1304 ppm
PROBHD	States-TFT1
T2 - Processing parameters	
SI	1304
SF	500.1300000 MHz
WDW	EM
SSB	QSBT
LB	2
GB	0
CB	0 Hz
PC	1.00
T3 - Processing parameters	
SI	1304
SI2	States-TFT1
SF2	500.1300000 MHz
WDW	EM
SSB	0 Hz
LB	0
GB	0