SUPPLEMENTARY MATERIAL

A New Cyclopeptide and A New Lignan from *Podocarpus neriifolius*

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Abstract:

A new cyclopeptide, neriitide A (**1**) and a new lignan, neriilignan (**2**), along with six known compounds including two diterpenoids, three sesquiterpenoids, and one sterol were isolated from the leaves of *Podocarpus neriifolius*. Their structures were elucidated by means of extensive spectroscopic analysis including HR-EI-MS, 1D- and 2D NMR techniques. This is the first report of cyclopeptide and lignan separated from this plant.

Keywords: *Podocarpus neriifolius*; Podocarpaceae; cyclopeptide; lignan

Supporting information

Spectroscopic data of the known compounds **3-8**.

Figure S1. Selected ^1H - ^1H COSY, HMBC and ROESY correlations of **1** and **2**.

Original spectra of compounds **1** and **2**.

^1H NMR Spectrum (500 MHz)

^{13}C NMR Spectrum (125 MHz)

COSY Spectrum

HSQC Spectrum

HMBC Spectrum

ROESY Spectrum

HREIMS

IR

Spectroscopic data of the known compounds 3-8.

Spatulenol (3)

Colorless oil, MF: C₁₅H₂₄O, MW: 220; ¹H-NMR (CD₃COCD₃, 500 MHz): δ 4.65 (1H, s, H-14b), 4.62 (1H, s, H-14a), 2.42 (1H, dd, *J* = 13.0, 6.0 Hz, H-4b), 2.17 (1H, m, H-6), 2.05 (1H, s, H-4a), 1.34 (1H, m, H-10), 1.24 (3H, s, H-15), 1.04 (3H, s, H-12), 1.02 (3H, s, H-13), 0.51 (1H, dd, *J* = 11.0, 9.5 Hz, H-1); ¹³C-NMR (CD₃COCD, 125 MHz): δ 154.9 (s, C-5), 106.6 (t, C-14), 80.6 (s, C-9), 54.9 (d, C-10), 54.8 (d, C-6), 42.9 (t, C-8), 40.0 (t, C-4), 31.4 (d, C-1), 29.3 (q, C-12), 28.4 (d, C-2), 27.8 (t, C-7), 26.9 (q, C-15), 25.9 (t, C-3), 21.1 (s, C-11), 16.9 (q, C-13).

4α,10α-epoxyaromadendrane (4)

yellow oil, MF: C₁₅H₂₄O, MW: 220; ¹H-NMR (CD₃OD, 500 MHz): δ 1.24 (3H, s, H-15), 1.16 (3H, s, H-14), 1.07 (3H, s, H-13), 1.05 (3H, s, H-12), 0.63 (1H, m, H-7), 0.46 (1H, m, H-6); ¹³C-NMR (CD₃OD, 125 MHz): δ 80.4 (s, C-10), 74.8 (s, C-4), 58.0 (d, C-5), 49.1 (d, C-1), 45.8 (t, C-3), 42.5 (t, C-9), 30.2 (d, C-6), 29.4 (q, C-12), 27.8 (d, C-7), 25.2 (t, C-8), 25.1 (q, C-15), 21.3 (t, C-2), 20.9 (s, C-11), 20.4 (q, C-14), 17.0 (q, C-13).

Blumenol C (5)

Yellow oil, MF: C₁₃H₂₂O₂, MW: 210; ¹H-NMR (CD₃OD, 500 MHz): δ 5.83 (1H, s, H-4), 3.72 (1H, m, H-9), 2.48 (1H, d, *J* = 17.5 Hz, H-2a), 2.06 (3H, s, H-13), 1.98 (1H, d, *J* = 17.5 Hz, H-2b), 1.97 (1H, m, H-6), 1.56 (2H, m, H-8), 1.70 (2H, m, H-7), 1.19 (3H, d, *J* = 6.5 Hz, H-10), 1.11 (3H, s, H-11), 1.04 (3H, s, H-12); ¹³C-NMR (CD₃OCD₃, 125 MHz): δ 202.7 (s, C-3), 170.2 (s, C-5), 125.7 (d, C-4), 69.2 (d, C-9), 52.7 (d, C-6), 48.4 (t, C-2), 40.1 (t, C-8), 37.6 (s, C-1), 29.3 (q, C-12), 27.7 (t, C-7), 27.7 (q, C-11), 25.2 (q, C-13), 23.8 (q, C-10).

$\Delta^{8,9}$ -isopimaric acid (6)

White amorphous powder, MF: C₂₀H₃₀O₂, MW: 302; ¹H-NMR (CD₃COCD₃, 500 MHz): δ 5.78 (1H, dd, J = 17.5, 10.5 Hz, H-15), 4.90 (1H, dd, J = 17.6, 1.2 Hz, H-16b), 4.84 (1H, dd, J = 10.7, 1.2 Hz, H-16a), 1.20 (3H, s, CH₃-19), 1.03 (3H, s, CH₃-17), 0.98 (3H, s, CH₃-20); ¹³C-NMR (CD₃COCD₃, 125 MHz): δ 183.2 (s, C-18), 147.4 (d, C-15), 138.2 (s, C-9), 126.1 (s, C-8), 111.8 (t, C-16), 49.2 (s, C-4), 48.0 (d, C-5), 43.1 (t, C-14), 38.4 (s, C-13), 38.3 (t, C-1), 37.3 (t, C-3), 36.5 (s, C-10), 36.3 (t, C-12), 33.3 (t, C-7), 29.0 (q, C-17), 23.0 (t, C-6), 22.5 (t, C-11), 20.3 (q, C-19), 19.6 (t, C-2), 17.3 (q, C-20).

Isopimaric acid (7)

White amorphous powder, MF: C₂₀H₃₀O₂, MW: 302; ¹H-NMR (CD₃OD, 500 MHz): δ 5.74 (1H, dd, J = 17.5, 11 Hz, H-15), 5.28 (1H, br d, J = 5.2 Hz, H-7), 4.88 (1H, dd, J = 17.6, 1.2 Hz, H-16b), 4.82 (1H, dd, J = 10.7, 1.2 Hz, H-16a), 1.17 (3H, s, CH₃-19), 1.01 (3H, s, CH₃-17), 0.96 (3H, s, CH₃-20); ¹³C-NMR (CD₃OD, 125 MHz): δ 184.1 (s, C-18), 146.1 (d, C-15), 136.4 (s, C-8), 124.6 (d, C-7), 110.8 (t, C-16), 49.4 (d, C-9), 47.4 (d, C-5), 46.1 (s, C-4), 41.9 (t, C-14), 36.8 (s, C-13), 36.7 (t, C-12), 35.5 (t, C-1), 35.0 (s, C-10), 34.9 (t, C-3), 27.8 (t, C-6), 21.6 (q, C-17), 21.0 (t, C-11), 19.6 (q, C-19), 18.1 (t, C-2), 16.2 (q, C-20).

5 α ,6 β -Dihydroxysitosterol (8)

White amorphous powder, MF: C₂₉H₅₂O₃, MW: 448; ¹H-NMR (CDCl₃, 500 MHz): δ 4.10 (1H, m, H-3), 3.54 (1H, s, H-6), 1.18 (3H, s, CH₃-19), 0.91 (3H, d, J = 6.5 Hz, CH₃-21), 0.85 (3H, t, J = 7.5 Hz, CH₃-29), 0.83 (3H, d, J = 7.0 Hz, CH₃-26), 0.81 (3H, d, J = 6.5 Hz, CH₃-27), 0.68 (3H, s, CH₃-18); ¹³C-NMR (CDCl₃, 125 MHz): δ 76.1 (s, C-5), 76.1 (d, C-6), 67.6 (d, C-3), 56.2 (d, C-17), 56.0 (d, C-14), 45.9 (d, C-24), 45.8 (d, C-9), 42.8 (s, C-13), 40.7 (t, C-12), 39.9 (t, C-4), 38.3 (s, C-10), 36.2 (d, C-20), 34.6 (t, C-22), 33.9 (t, C-2), 32.4 (t, C-1), 30.9 (t, C-7), 30.2 (d, C-25), 29.2 (d, C-8), 28.2 (t, C-16), 26.1 (t, C-23), 24.2 (t, C-15), 23.1 (t, C-28), 21.2 (t, C-11), 19.8 (q, C-27), 19.0 (q, C-26), 18.7 (q, C-21), 16.9 (q, C-19), 12.2 (q, C-29), 12.0 (q, C-18).

Figure S1. Selected ^1H - ^1H COSY, HMBC and ROESY correlations of 1 and 2.

Original spectra of compound 1.

¹HNMR (CDCl₃):

¹³CNMR(CDCl₃):

Current Data Parameters
NAME WJY-33
PROCNO 11
PROCNO 11
F2 - Acquisition Parameters
Date_ 20131022
Time 22.32
INSTRUM spect
PROBHD 5 mm PABBO BBO
PULPROG zgpg30
TD 65536
SOLVENT CDCl₃
NS 1024
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.105942 sec
RG 197.02
WDW 16.800 usec
DE 6.50 usec
TE 300.8 K
D1 2.00000000 sec
D11 0.03000000 sec

CHANNEL f1 13C
NUC1 P1 13.49 usec
PL1 53.7029911 W
SFO1 125.7703637 MHz

CHANNEL f2 13C
NUC2 P2 13.49 usec
PL2 53.7029911 W
SFO2 125.7703637 MHz

F2 - Processing Parameters
SI 32768
SF 125.7577890 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

H-H COSY:

HSQC:

HMBC-1:

HMBC-2

ROESY:

Elemental Composition Report

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -10.0, max = 120.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
24 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)
Elements Used:
C: 0-200 H: 0-400 N: 4-4 O: 4-6
NWJL-33
16:03:42 15-Apr-2014
Voltage EI+
KIB
M140415EA-07AFAMM 13 (1.193)
620.2994

Autospec Premier
P776
212

Minimum:					
Maximum:					
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT Formula
620.2994	620.2999	-0.5	-0.8	20.0	5546126.5 C37 H40 N4 O5

HREIMS:

IR:

Original spectra of compound **2**.

^1H NMR (DMSO):

^{13}C NMR(CDCl_3):

H-H COSY:

HSQC:

HMBC:

ROESY:

HREIMS:

Elemental Composition Report

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -10.0, max = 120.0
Selected filters: None

Monoisotopic Mass, Odd and Even Electron Ions
17 formula(e) evaluated with 1 results within limits (up to 51 closest results for each mass)

Elements Used:

C: 0-200 H: 0-400 O: 5-7

NWUJ-9

15-57:02 15-Apr-2014

Voltage EI+

KIB
M140415EA-01AFAMM 18 (1.653)
360.1559

Autospec Premier
P776
5.31

Minimum: -10.0
Maximum: 120.0

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
360.1559	360.1573	-1.4	-3.9	9.0	5546025.5	C20 H24 O6

IR:

E:\DATA\2014\05\20\1.9 1 sample form

20/05/2014