SUPPLEMENTARY MATERIAL

A New Cyclopeptide and A New Lignan from Podocarpus nerifolius

Jingjing Wu, Haoliang Li, Guoli Huang, and Yegao Chen*

School of Chemistry and Chemical Engineering, Yunnan Normal University, Kunming 650500, China

*Corresponding authors. Tel: 86-871-65941089; Email: yegaochen@ynnu.edu.cn

Abstract:
A new cyclopeptide, neritide A (1) and a new lignan, nerilignan (2), along with six known compounds including two diterpenoids, three sesquiterpenoids, and one sterol were isolated from the leaves of Podocarpus nerifolius. 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 nerifolius; Podocarpaceae; cyclopeptide; lignan
Supporting information

Spectroscopic data of the known compounds 3-8.

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

Original spectra of compounds 1 and 2.

$^1$H 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: C_{15}H_{24}O, MW: 220; $^1$H-NMR (CD$_3$COCD$_3$, 500 MHz): $\delta$ 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), 0.51 (1H, dd, $J = 11.0$, 9.5 Hz, H-1); $^{13}$C-NMR (CD$_3$COCD$_3$, 125 MHz): $\delta$ 154.9 (s, C-5), 106.6 (t, C-14), 80.6 (s, C-9), 54.9 (d, C-6), 54.8 (d, C-10), 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: C_{13}H_{24}O, MW: 220; $^1$H-NMR (CD$_3$OD, 500 MHz): $\delta$ 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); $^{13}$C-NMR (CD$_3$OD, 125 MHz): $\delta$ 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: C_{13}H_{22}O$_2$, MW: 210; $^1$H-NMR (CD$_3$OD, 500 MHz): $\delta$ 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); $^{13}$C-NMR (CD$_3$OCD$_3$, 125 MHz): $\delta$ 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).
**A^8,9-isopimaric acid (6)**

White amorphous powder, MF: C_{20}H_{30}O_{2}, MW: 302; ^1H-NMR (CD$_3$COCD$_3$, 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, CH$_3$-19), 1.03 (3H, s, CH$_3$-17), 0.98 (3H, s, CH$_3$-20); ^13C-NMR (CD$_3$COCD$_3$, 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: C_{20}H_{30}O_{2}, MW: 302; ^1H-NMR (CD$_3$OD, 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, CH$_3$-19), 1.01 (3H, s, CH$_3$-17), 0.96 (3H, s, CH$_3$-20); ^13C-NMR (CD$_3$OD, 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).

**5α,6β-Dihydroxysitosterol (8)**

White amorphous powder, MF: C_{29}H_{52}O_{3}, MW: 448; ^1H-NMR (CDCl$_3$, 500 MHz): δ 4.10 (1H, m, H-3), 3.54 (1H, s, H-6), 1.18 (3H, s, CH$_3$-19), 0.91 (3H, d, J = 6.5 Hz, CH$_3$-21), 0.85 (3H, t, J = 7.5 Hz, CH$_3$-29), 0.83 (3H, d, J = 7.0 Hz, CH$_3$-26), 0.81 (3H, d, J = 6.5 Hz, CH$_3$-27), 0.68 (3H, s, CH$_3$-18); ^13C-NMR (CDCl$_3$, 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 $^1$H-$^1$H COSY, HMBC and ROESY correlations of 1 and 2.
Original spectra of compound 1.

$^1$HNMR (CDCl$_3$):
$^{13}$CNMR(CDCl$_3$):
H-H COSY:
HSQC:
| Component | Mass (amu) | Relative Abundance (%) |
|-----------|------------|------------------------|
| H          | 1.0        | 1.0                    |
| O          | 16.0       | 16.0                   |

**Elemental Composition Report**

- **Elements Used:**
  - C: 0.2%, H: 0.4%, N: 44.0%, O: 44.0%
- **Monotonic Mass, Odd and Even Electron Ions**
- **Tolerances:**
  - D.E.: Min = 10.0, Max = 120.0
  - Tolerance = 10.0 Ppm
- **Selected Ions:** None
Original spectra of compound 2.

$^1$HNMR (DMSO):
$^1$H NMR (CDCl$_3$):
H-H COSY:
HSQC:
HMBC:
# 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: 0-7

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**Autospec Premier**

**P976**

**5.31**

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| 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: