Supplementary Information

New bioactive cyclopeptide alkaloids with rare terminal unit from the root bark of *Ziziphus cambodiana*

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Figure S1 ¹H NMR spectrum of cambodine A (1) in DMSO- d_6 at 300 MHz



Figure S2 13 C NMR spectrum of cambodine A (1) in DMSO- d_6 at 75 MHz



Figure S3 DEPT and ¹³C NMR spectra of cambodine A (1) in DMSO- d_6



Figure S4 COSY spectrum of cambodine A (1) in DMSO- d_6



Figure S5 HMQC spectrum of cambodine A (1) in DMSO- d_6



Figure S6 HMBC spectrum of cambodine A (1) in DMSO- d_6



Figure S7 NOESY spectrum of cambodine A (1) in DMSO- d_6



Figure S8 1 H NMR spectrum of cambodine C (2) in CDCl₃ at 300 MHz





Figure S10 DEPT and 13 C NMR spectra of cambodine C (2) in CDCl₃ at 75 MHz



Figure S11 COSY spectrum of cambodine C (2) in CDCl₃



Figure S12 HMQC spectrum of cambodine C (2) in CDCl₃



Figure S13 HMBC spectrum of cambodine C (2) in $CDCl_3$



Figure S14 NOESY spectrum of cambodine C (2) in $CDCl_3$



Figure S15 ¹H NMR spectrum of cambodine C (2) in DMSO- d_6 at 300 MHz



Figure S16¹³C NMR spectrum of cambodine C (**2**) in DMSO-d₆ at 75 MHz



Figure S17 DEPT and ¹³C NMR spectra of cambodine C (2) in DMSO- d_6 at 75 MHz

DEPT135



Figure S18 COSY spectrum of cambodine C (2) in DMSO- d_6



Figure S19 HMQC spectrum of cambodine C (2) in DMSO- d_6



Figure S20 HMBC spectrum of cambodine C (2) in DMSO- d_6



Figure S21 NOESY spectrum of cambodine C (2) in DMSO- d_6



Figure S22 ¹H NMR spectrum of cambodine F (**3**) in CDCl₃ at 300 MHz



Figure S23 13 C NMR spectrum of cambodine F (3) in CDCl₃ at 75 MHz



Figure S24 DEPT and ¹³C NMR spectra of cambodine F (**3**) in CDCl₃ at 75 MHz



Figure S25 COSY spectrum of cambodine F (3) in CDCl₃



Figure S26 HMQC spectrum of cambodine F(3) in $CDCl_3$



Figure S27 HMBC spectrum of cambodine F (3) in CDCl₃



Figure S28 NOESY spectrum of cambodine F (3) in CDCl₃



Figure S29 ¹H NMR spectrum of cambodine B (4) in CDCl₃ at 300 MHz



Figure S30 ¹³C NMR spectrum of cambodine B (4) in CDCl₃ at 75 MHz



Figure S31 DEPT and ¹³C NMR spectra of cambodine B (4) in CDCl₃



Figure S32 COSY spectrum of cambodine B (4) in CDCl₃



Figure S33 HMQC spectrum of cambodine B (4) in CDCl₃



Figure S34 HMBC spectrum of cambodine B (4) in $CDCl_3$



Figure S35 NOESY spectrum of cambodine B (4) in $CDCl_3$



Figure S36 ¹H NMR spectrum of cambodine D (**5**) in CDCl₃ at 300 MHz



Figure S37 13 C NMR spectrum of cambodine D (5) in CDCl₃ at 75 MHz



Figure S38 DEPT and ¹³C NMR spectra of cambodine D (5) in CDCl₃



Figure S39 COSY spectrum of cambodine D (5) in CDCl₃



Figure S40 HMQC spectrum of cambodine D (5) in CDCl₃



Figure S41 HMBC spectrum of cambodine D (5) in CDCl₃



Figure S42 NOESY spectrum of cambodine D(5) in $CDCl_3$



Figure S43 1 H NMR spectrum of cambodine E (6) in CDCl₃ at 300 MHz



Figure S44 13 C NMR spectrum of cambodine E (6) in CDCl₃ at 75 MHz



Figure S45 DEPT and ¹³C NMR spectra of cambodine E (6) in CDCl₃



Figure S46 COSY spectrum of cambodine E (6) in $CDCl_3$



Figure S47 HMQC spectrum of cambodine E (6) in CDCl₃



Figure S48 HMBC spectrum of cambodine E (6) in $CDCl_3$



Figure S49 NOESY spectrum of cambodine E (6) in CDCl₃



Figure S50 ¹H NMR spectrum of frangufoline (7) in CDCl₃ at 300 MHz



Figure S51 13 C NMR spectrum of frangufoline (7) in CDCl₃ at 75 MHz



Figure S52 ¹H NMR spectrum of lotusanine B (8) in CDCl₃ at 300 MHz



Figure S53 ¹³C NMR spectrum of lotusanine B (8) in CDCl₃ at 75 MHz



¹H and ¹³C NMR spectroscopic data of frangufoline (7) and (–) lotusanine B (8)

Frangufoline (7): ¹H NMR (300 MHz, CDCl₃) $\delta_{\rm H}$ 7.90 (1H, d, J = 10.0 Hz, NH-24), 7.26 (2H, overlapping signal, H-29, 29'), 7.25 (2H, overlapping signal, H-30,30'), 7.22 (1H, overlapping signal, H-31), 7.19 (1H, overlapping signal, H-16), 7.13 (1H, overlapping signal, H-12), 7.07 (1H, overlapping signal, H-15), 7.04 (1H, overlapping signal, H-13), 6.67 (1H, dd, J = 10.6, 7.5 Hz, H-2), 6.46 (1H, d, J = 10.6 Hz, H-3), 6.36 (1H, d, J = 7.5 Hz, H-1), 5.78 (1H, d, J = 7.9 Hz, NH-6), 5.00 (1H, dd, J = 7.1, 1.5 Hz, H-9), 4.50 (1H, dd, J = 10.0, 7.1 Hz, H-8), 4.04 (1H, ddd, J = 11.3, 7.9, 3.3 Hz, H-5), 3.21 (1H, m, H-26), 3.18 (1H, m, H-27a), 2.85 (1H, dd, J = 15.8, 8.3 Hz, H-27b), 2.24 (6H, s, NMe₂), 1.93 (1H, m, H-21), 1.68 (1H, ddd, J = 14.3, 11.3, 3.3 Hz, H-17a), 1.29 (3H, d, J = 6.7 Hz, H-23), 1.24 (1H, overlapping signal, H-17b), 1.10 (1H, m, H-18), 1.01 (3H, d, J = 6.7 Hz, H-22), 0.65 (3H, d, J = 6.6 Hz, H-19), 0.60 (3H, d, J = 6.6 Hz, H-20); ¹³C NMR (75 MHz, CDCl₃) $\delta_{\rm C}$ 172.6 (C-25), 171.6 (C-7), 167.4 (C-4), 155.9 (C-11), 140.3 (C-28), 131.7 (C-15), 131.8 (C-14), 130.2 (C-13), 128.9 (C-30, 30'), 128.5 (C-29, 29'), 126.1 (C-31), 125.6 (C-2), 122.7 (C-16), 123.0 (C-12), 115.6 (C-1), 81.7 (C-9), 70.4 (C-26), 55.2 (C-8), 52.6 (C-5), 41.8 (NMe₂), 39.1 (C-17), 30.6 (C-27), 29.3 (C-21), 24.3 (C-19), 23.1 (C-18), 20.4 (C-20), 20.3 (C-22), 15.0 (C-23).

(-) Lotusanine B (8): ¹H (300MHz, CDCl₃) δ_H 8.09 (1H, d, J = 9.4 Hz, NH-24), 7.73 (1H, d, J = 15.4 Hz, H-33), 7.56 (2H, dd, J = 7.2, 2.0 Hz, H-35, H-35'), 7.41 (2H, t, J = 7.2 Hz, H-36, H-36'),
7.27 (2H, overlapping signal, H-18, H-18'), 7.22 (1H, overlapping signal, H-12), 7.17 (1H,

overlapping signal, H-16), 7.07 (2H, overlapping signal, H-19, H-19'), 7.05 (1H, overlapping signal, H-15), 7.04 (1H, overlapping signal, H-13), 7.02 (2H, overlapping signal, H-20, H-37), 6.73 (1H, dd, J = 10.4, 7.5 Hz, H-2), 6.69 (1H, d, J = 15.4 Hz, H-32), 6.56 (1H, d, J = 10.4 Hz, NH-3), 6.36 (1H, d, J = 7.5 Hz, H-1), 6.09 (1H, d, J = 7.5 Hz, NH-6), 4.94 (1H, dd, J = 6.6, 1.6 Hz, H-9), 4.61 (1H, ddd, J = 10.9, 7.5, 3.3 Hz, H-5), 4.32 (1H, dd, J = 9.4, 6.6 Hz, H-8), 4.16 (1H, d, J = 7.6 Hz, H-26), 3.58 (2H, m, H-29), 3.42 (1H, dd, J = 15.6, 3.3 Hz, H-17a), 2.75 (1H, dd, J = 15.6, 10.9 Hz, H-17b), 2.26 (1H, dd, J = 12.2, 4.4, Hz, H-27a), 2.03 (2H, m, H-28), 1.82 (1H, m, H-21), 1.56 (1H, m, H-27b), 1.14 (3H, d, J = 6.7 Hz, H-23), 0.69 (3H, d, J = 6.6 Hz, H-22); ¹³C NMR (75 MHz, CDCl₃) $\delta_{\rm C}$ 171.4 (C-25), 171.1 (C-7), 166.9 (C-4), 166.5 (C-31), 156.0 (C-11), 144.1 (C-33), 136.6 (C-14, C-18a), 134.6 (C-34), 131.8 (C-15), 130.3 (C-37), 130.1 (C-20), 128.9 (C-36, C-36'), 128.5 (C-35, C-35'), 128.2 (C-18, C-18'), 128.0 (C-19, C-19'), 126.5 (C-13), 125.5 (C-2), 123.4 (C-16), 123.4 (C-12), 116.9 (C-32), 115.5 (C-1), 81.8 (C-9), 59.1 (C-26), 55.1 (C-8), 53.4 (C-5), 47.1 (C-29), 35.9 (C-17), 29.0 (C-21), 25.8 (C-27), 24.9 (C-28), 20.4 (C-23), 14.5 (C-22).















Figure S57 CD spectrum of cambodine B (4) in MeOH



Figure S59 CD spectrum of cambodine E (6) in MeOH