

Physico-chemical properties of compound 1 and 2

PF1171A (**1**): white solid; $[\alpha]_{589}^{25} +31^\circ$ (c 0.15, MeOH); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 0.87 (3H, d, $J = 6.0$ Hz, Leu- δ), 0.90 (3H, d, $J = 7.2$ Hz, *allo*-Ile- γ), 0.91 (3H, t, $J = 7.2$ Hz, *allo*-Ile- δ), 0.94 (3H, d, $J = 5.2$ Hz, Leu- δ'), 0.95, (3H, d, $J = 7.2$ Hz, MeLeu- δ'), 0.97 (3H, d, $J = 6.8$ Hz, MeLeu- δ), 1.27 (3H, d, $J = 6.8$ Hz, Ala- β), 1.38 (2H, m, *allo*-Ile- γ'), 1.53 (1H, m, Leu- γ), 1.57 (2H, m, Pip- γ), 1.63 (1H, m, MeLeu- γ), 1.76 (2H, m, Leu- β , Pip- β), 1.91 (1H, m, MeLeu- β), 1.98 (1H, m, Leu- β), 2.04 (3H, m, Pip- β , Pip- δ), 2.18 (1H, m, MeLeu- β), 2.41 (1H, m, *allo*-Ile- β), 3.14 (1H, d, $J = 3.0$ Hz, Pip- ϵ), 3.17 (3H, s, MeLeu-*N*-Me), 3.47 (1H, m, MeLeu- α), 3.67 (1H, dd, $J = 3.0, 11.5$ Hz, Pip- α), 4.12 (1H, d, $J = 13.5$ Hz, Pip- ϵ), 4.43 (1H, dd, $J = 3.0, 7.5$ Hz, *allo*-Ile- α), 4.53 (1H, m, Leu- α), 4.80 (1H, m, Ala- α), 7.11 (1H, t, $J = 7.5$ Hz ABA-3), 7.18 (1H, d, $J = 7.5$ Hz, ABA-5), 7.39 (1H, d, $J = 7.5$ Hz, ABA-2), 7.46 (1H, t, $J = 13.5$ Hz, ABA-4), 7.62 (1H, d, $J = 9.5$ Hz, Ala-NH), 7.99 (1H, d, $J = 8.0$ Hz, Leu-NH), 8.30 (1H, d, $J = 8.5$ Hz, *allo*-Ile-NH), 9.43(1H, s, ABA-NH). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 11.9 (*allo*-Ile- δ), 14.0 (*allo*-Ile- γ), 18.5 (Ala- β), 21.8 (Leu- δ), 22.1 (MeLeu- δ), 23.2 (Leu- δ'), 23.4 (MeLeu- δ'), 24.5 (Leu- γ , Pip- β), 25.6 (MeLeu- γ), 26.9 (*allo*-Ile- γ'), 27.4 (Pip- γ), 28.1 (Pip- δ), 36.3 (Leu- β), 36.5 (*allo*-Ile- α), 37.8 (MeLeu- β), 37.9 (MeLeu-*N*-Me), 47.9 (Ala- α), 50.9 (Leu- α), 52.7 (Pip- ϵ), 57.3 (*allo*-Ile- α), 61.6 (Pip- α), 65.2 (MeLeu- α), 122.7 (ABA-1), 123.3 (ABA-3), 123.9 (ABA-2), 127.2 (ABA-5), 131.8 (ABA-4), 137.2 (ABA-6), 168.9 (Pip-CO), 169.3 (MeLeu-CO), 170.3 (ABA-CO), 171.1 (*allo*-Ile-CO), 174.1 (Leu-CO), 174.4 (Ala-CO).

PF1171C (**2**): white solid; $[\alpha]_{589}^{25} +26^\circ$ (c 0.15, MeOH); $^1\text{H-NMR}$ (500 MHz, CDCl_3) δ : 0.87 (3H, d, $J = 6.0$ Hz, Leu- δ), 0.93 (3H, d, $J = 7.2$ Hz, Val- γ), 0.96 (6H, d, $J = 6.8$ Hz, I6.8 Hz, MeLeu- δ' , Leu- δ), 0.97 (3H, d, $J = 6.8$ Hz, MeLeu- δ), 1.05, (3H, d, $J = 7.2$ Hz, Val- γ'), 1.28 (3H, d, $J = 6.8$ Hz, Ala- β), 1.54 (3H, m, Leu- γ , Pip- δ), 1.63 (1H, m, MeLeu- γ), 1.74 (1H, m, Pip- β), 1.76 (1H, m, Leu- β), 1.91 (1H, m, MeLeu- β), 2.00 (1H, m, Leu- β), 2.04 (1H, m, Pip- β), 2.08 (2H, m, Pip- γ), 2.17 (1H, m, MeLeu- β), 2.67 (1H, m, Val- β), 3.14 (1H, d, $J = 3.0$ Hz Pip- ϵ), 3.18 (3H, s, MeLeu-*N*-Me), 3.47 (1H, dd, $J = 5.0, 9.0$ Hz, MeLeu- α), 3.67 (1H, dd, $J = 3.0, 11.5$ Hz, Pip- α), 4.12 (1H, d, $J = 13.5$ Hz, Pip- ϵ), 4.30 (1H, dd, $J = 3.0, 7.5$ Hz, Val- α), 4.55 (1H, m, Leu- α), 4.80 (1H, m, Ala- α), 7.11 (1H, t, $J = 7.5$ Hz ABA-3), 7.18 (1H, d, $J = 7.5$ Hz, ABA-5), 7.45 (1H, t, $J = 13.5$ Hz, ABA-4), 7.62 (1H, d, $J = 9.5$ Hz, Ala-NH), 7.99 (1H, d, $J = 8.0$ Hz, Leu-NH), 8.28 (1H, d, $J = 8.0$ Hz, Val-NH), 9.39(1H, s, ABA-NH). $^{13}\text{C-NMR}$ (125 MHz, CDCl_3) δ : 16.2 (Val- γ), 18.4 (Ala- β), 19.8 (Ala- γ'), 21.8 (Leu- δ), 22.1 (MeLeu- δ)

23.2 (Leu- δ'), 23.3 (MeLeu- δ'), 24.4 (Leu- γ), 24.5 (Pip- β), 25.6 (MeLeu- γ), 27.4 (Pip- δ), 28.2 (Pip- γ), 29.9 (Val- δ) 36.3 (Leu- β), 37.8 (MeLeu- β), 37.9 (MeLeu-*N*-Me), 47.9 (Ala- α), 50.9 (Leu- α), 52.7 (Pip- ϵ), 59.2 (Val- α), 61.6 (Pip- α), 65.2 (MeLeu- α), 122.8 (ABA-1), 123.3 (ABA-3), 123.9 (ABA-2), 127.2 (ABA-5), 131.8 (ABA-4), 137.2 (ABA-6), 168.9 (Pip-CO), 169.3 (MeLeu-CO), 170.2 (ABA-CO), 170.7 (Val-CO), 174.2 (Leu-CO), 174.4 (Ala-CO).