Supporting Information

Pteratides I - IV, New Cytotoxic Cyclodepsipeptides from the Malaysian Basidiomycete *Pterula* sp.

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List of Supporting information

General experimental procedures	S3
Table T1. NMR data (CDCl ₃ at 23° C) for pteratide I (1).	S4
Table T2. NMR data (MeOH- <i>d</i> ₄ at 23° C) for pteratide II (2).	S6
Table T3. NMR data (MeOH- <i>d</i> ₄ at 23° C) for pteratide III (3).	S8
Table T4. NMR data (CDCl ₃ at 23° C) for pteratide IV (4).	S9
S1. ¹ H NMR spectrum of pteratide I (1) in CDCl ₃ .	S11
S2. ¹³ C NMR spectrum of pteratide I (1) in CDCl ₃ .	S12
S3. COSY spectrum of pteratide I (1) in CDCl ₃ .	S13
S4. TOCSY spectrum of pteratide I (1) in CDCl ₃ .	S14
S5. NOESY spectrum of pteratide I (1) in CDCl ₃ .	S15
S6. HSQC-DEPT spectrum of pteratide I (1) in CDCl ₃ .	S16

S7. HMBC-CIGAR spectrum of pteratide I (1) in CDCl ₃ .	S17
S8. IMPRESS spectrum of pteratide I (1) in CDCl ₃ .	S18
S9. ¹ H NMR spectrum of pteratide II (2) in MeOH- <i>d</i> ₄ .	S19
S10. ¹³ C NMR spectrum of pteratide II (2) in MeOH- <i>d</i> ₄ .	S20
S11. COSY spectrum of pteratide II (2) in MeOH- <i>d</i> ₄ .	S21
S12. TOCSY spectrum of pteratide II (2) in MeOH- <i>d</i> ₄ .	S22
S13. NOESY spectrum of pteratide II (2) in MeOH- <i>d</i> ₄ .	S23
S14. HSQC-DEPT spectrum of pteratide II (2) in MeOH- <i>d</i> ₄ .	S24
S15. HMBC-CIGAR spectrum of pteratide II (2) in MeOH- <i>d</i> ₄ .	S25
S16. IMPRESS spectrum of pteratide II (2) in MeOH- <i>d</i> ₄ .	S26
S17. ¹ H NMR spectrum of pteratide III (3) in MeOH- <i>d</i> ₄ .	S27
S18. COSY spectrum of pteratide III (3) in MeOH- <i>d</i> ₄ .	S28
S19. TOCSY spectrum of pteratide III (3) in MeOH- <i>d</i> ₄ .	S29
S20. HSQC-DEPT spectrum of pteratide III (3) in MeOH- <i>d</i> ₄ .	S30
S21. HMBC-CIGAR spectrum of pteratide III (3) in MeOH- <i>d</i> ₄ .	S31
S22. ¹ H NMR spectrum of pteratide IV (4) in CDCl ₃ .	S32
S23. ¹³ C NMR spectrum of pteratide IV (4) in CDCl ₃ .	S33
S24. COSY spectrum of pteratide IV (4) in CDCl ₃ .	S34
S25. TOCSY spectrum of pteratide IV (4) in CDCl ₃ .	S35
S26. ROESY spectrum of pteratide IV (4) in CDCl ₃ .	S36
S27. HSQC-DEPT spectrum of pteratide IV (4) in CDCl ₃ .	S37
S28. HMBC-CIGAR spectrum of pteratide IV (4) in CDCl ₃ .	S38
S29. IMPRESS spectrum of pteratide IV (4) in CDCl ₃ .	S39
S30. ESI MS/MS for pteratide I methyl ester.	S40
S31. ESI MS/MS for pteratide II methyl ester.	S41
Table T5. HPLC analysis of FDAA-derivatized acid hydrolysates of pteratides I- IV (1-4).	S42

General Experimental Procedures.

NMR spectra were recorded at 500 MHz and 125 MHz for ^1H and ^{13}C NMR, respectively, using the signals of the residual solvent protons (CDCl_3 : δ 7.25, $\text{MeOH}-d_4$: δ 3.3) and the solvent carbons (CDCl_3 : δ 77.01, $\text{MeOH}-d_4$: 49.3) as internal references. Solvents used for extraction and isolation were distilled prior to use. Standard protocols were used in cytotoxicity assay (Alley, M. C.; Scudiero, D. A.; Monks, A.; Hursey, M. L.; Czerwinski, M. J.; Fine, D. L.; Abbott, B. J.; Mayo, J. G.; Shoemaker, R. H.; Boyd, M. R. *Cancer Res.* 1988, 48, 589-601).

Isolation of pteratide I (1). The extract from thallus A (30 mg) was subjected to flash chromatography on an ODS phase, eluting with increasing concentrations of MeOH in H_2O . The fractions eluted with MeOH were dried and then further purified by semi-preparative HPLC (Luna C18, 10 x 250 mm, 5 μm) under isocratic conditions ($\text{MeCN}-\text{H}_2\text{O}$ (6:4), flow: 5 mL min^{-1} ; UV detection at 210 nm); compound **1** (0.9 mg) was eluted after 16 min. In all following purification procedures by semi-preparative HPLC the same column and flow rate were used.

Isolation of pteratides II (2) and III (3). The extract from thallus B (1 g) was partitioned between petroleum ether and $\text{MeOH}-\text{H}_2\text{O}$ (99:1, v/v). The MeOH phase was taken to dryness (850 mg) and purified further by isocratic semi-preparative HPLC using $\text{MeCN}-\text{H}_2\text{O}$ (13:7) as the eluent. The peak at 12 min was collected and, after evaporation of the solvent (14.4 mg), further purified by semi-preparative HPLC using $\text{MeCN}-(\text{H}_2\text{O} + 0.05\% \text{ TFA})$ (1:1) to give **2** (1.3 mg). The peak at 18 min (9.6 mg) was likewise subjected to further semi-preparative HPLC using $\text{MeCN}-(\text{H}_2\text{O} + 0.05\% \text{ TFA})$ (11:9) yielding **3** (7.1 mg).

Isolation of pteratide IV (4). The extract from thallus C (110 mg) was partitioned between petroleum ether and $\text{MeOH}-\text{H}_2\text{O}$ (95:5, v/v). The MeOH phase was dried and partitioned between EtOAc (100 mL) and H_2O (100 mL). Preparative HPLC of the dried EtOAc phase (91 mg) (column: ODS 19 300 mm; solvents: $\text{H}_2\text{O} + 0.05\% \text{ TFA}$ (A), MeCN (B); gradient: 0 min - 75% B, 15 min - 100% B; 11 mL/min) yielded **4** (4.9 mg; t_{r} 14 min) and more pteratide I (**1**; 2.0 mg; t_{r} 12 min).

Table T1. NMR data (CDCl₃ at 23° C) for pteratide I (1).

Position	¹³ C [ppm]	¹ H [ppm, mult. ^a Hz]	COSY	HMBC	ROESY
<i>Thr</i>					
NH		7.24 <i>ol</i>	2	1, Bz-1	NMe, 2, Bz-3/7, Val2-3, Val2-4, Val2-5
1	168.9				
2	52.2	5.33 <i>d</i> 8.6	NH	1, Bz-1	NH, 3, 4, Ala1-NMe, Leu-NMe
3	73.0	5.12 <i>ol</i>	4	1, Val2-1	2, Ala1-3, Val1-3, Ala1-NMe, Leu-NMe
4	18.1	1.39 <i>s</i>	3	2, 3	NH, 2, Bz-3/7, Val2-NMe
Bz-1	167.7				
Bz-2	133.8				
Bz-3/7	127.5	7.85 <i>d</i> 7.7	Bz-4/6	Bz-1, Bz-3/7, Bz-5	NH, 4, Val2-3, Val2-4, Val2-5
Bz-4/6	132.5	7.50 <i>t</i> 7.4	Bz-3/7, Bz-5	Bz-2, Bz-3/7, Bz-4/6	
Bz-5	129.1	7.58 <i>t</i> 7.4	Bz-4/6	Bz-3/7	
<i>Leu</i>					
NMe	30.6	2.91 <i>s</i>		2, Thr-1	3a, 3b, Ala1-3, Thr-2, Thr-3
1	169.2				
2	53.6	5.28 <i>dd</i> 6.4, 5.4	3a, 3b	NMe, 1, 3	NMe, 3a, 3b, 4, 5, 6, Val2-4, Ala1-NMe, Ala1-2
3	37.5	1.34 <i>ol</i>	2, 3b	1, 2, 6	NMe, 2, 3b, 5
		1.97 <i>m</i>	2, 3a	2, 6	NMe, 2, 3a, 4, 6
4	25.0	1.50 <i>m</i>	5, 6		NMe, 2, 3b, 5
5	22.5	0.91 <i>ol</i>	4	3, 4, 6	2, 3a, 4
6	23.2	0.93 <i>ol</i>	4	3, 4, 5	3b
<i>Ala1</i>					
NMe	29.3	2.58 <i>s</i>		2, Leu-1	2, 3, Val2-NMe, Val2-2, Val2-4, 4-MePro-5a, Phe-3b, Thr-3, Leu-2
1	168.6				
2	52.0	5.48 <i>q</i> 6.3	3	NMe, 1, 3	NMe, 3, 4-MePro-5a, 4-MePro-5b
3	14.4	1.25 <i>d</i> 6.2	2	1, 2	NMe, 2, Leu-NMe, Phe-3b, Phe-5/9
<i>4-MePro</i>					
1	171.8				
2	56.4	4.90 <i>dd</i> 8.1, 4.5	3a, 3b		3a, 3b, 5a, 4-Me, Ala1-NMe, Ala2-2, Phe-NH
3	36.0	1.79 <i>m</i>	1, 3b	1, 4-Me	2, 3b, 4, 5a, 4-Me
		2.06 <i>m</i>	1, 3a	1	2, 3a, 4, 5b, 4-Me, Ala2-2
4	33.5	2.75 <i>m</i>	5b, 4-Me		3a, 3b, 5b, 4-Me
5	54.0	2.93 <i>dd</i> 10.2, 6.8	5b	3, 4, 4-Me	5b, 4-Me, Ala1-2
		3.89 <i>dd</i> 10.2, 6.9	4, 5a	3, 4, 4-Me	3b, 4, 5a, 4-Me, Ala1-2
4-Me	17.9	1.03 <i>d</i> 6.9	4	3, 4, 5	2, 3a, 3b, 4, 5a, 5b, Ala1-NMe
<i>Ala2</i>					
NMe	29.0	2.50 <i>s</i>		2, 4-MePro-1	2, 3, Phe-NH, Phe-5/9, Phe-6/8
1	170.7				
2	56.2	4.63 <i>ol</i>	3	NMe, 1, 3, 4-MePro-1	NMe, 3, 4-MePro-2, 4-MePro-3a, 4-MePro-3b, Phe-NH
3	15.0	1.33 <i>d</i> 7.0	2	1, 2	NMe, 2
<i>Phe</i>					
NH		9.31 <i>d</i> 7.2	2	Ala2-1	3, 5/9, Ala1-NMe, Ala2-NMe, Ala2-2, 4-MePro-2
1	172.3				
2	54.5	4.60 <i>ol</i>	NH, 3b		3a, 3b, 5/9, Val1-NMe
3	35.0	3.05 <i>dd</i> 14.4, <2	3b	4, 5	2, 3b, 5/9, Val1-NMe
		3.37 <i>dd</i> 14.4, 12.0	2, 3a	4, 5	NH, 2, 3a, 5/9, Ala1-NMe, Ala1-3
4	139.0				
5/9	129.5	7.41 <i>d</i> 7.3	6/8	3, 5/9, 7	NH, 2, 3a, 3b, 6/8, Ala2-NMe, Ala1-3, Val1-NMe
6/8	128.7	7.26 <i>t</i> 7.5	5/9, 7	4, 5/9, 6/8	5/9, Ala2-NMe
7	126.9	7.19 <i>t</i> 7.5	6/8		6/8

^aol = overlapping signals

Table T1. NMR data (CDCl₃ at 23° C) for pteratide I (**1**) (cont.)

Position	¹³ C [ppm]	¹ H [ppm, mult. ^a Hz]	COSY	HMBC	ROESY
<i>Val1</i>					
NMe	29.9	3.24 <i>s</i>		2, <i>Phe</i> -1	2, 3, 4, <i>Phe</i> -2, <i>Phe</i> -3a, <i>Phe</i> -5/9
1	171.1				
2	57.7	5.10 <i>ol</i>	3	NMe, 1, 3, 4, <i>Phe</i> -1	NMe, 3, 4, 5, <i>Val</i> 2-2, <i>Val</i> 2-3, <i>Val</i> 2-4, <i>Val</i> 2-5
3	27.6	2.45 <i>m</i>	2, 4, 5		NMe, 2, 4, 5
4	18.5	0.92 <i>ol</i>	3	2, 3, 5	NMe, 2, 3, <i>Leu</i> -2
5	20.2	0.88 <i>d</i> 6.5	3	2, 3, 4	2, 3, <i>Val</i> 2-NMe, <i>Val</i> 2-4
<i>Val2</i>					
NMe	29.7	2.71 <i>s</i>		2, <i>Val</i> 1-1	2, 3, 4, 5, <i>Val</i> 1-NMe, <i>Val</i> 1-2, <i>Val</i> 1-5, <i>Thr</i> -4
1	168.7				
2	66.2	4.88 <i>ol</i>	3	NMe, 1, 4, <i>Val</i> 1-1	NMe, 3, 4, 5, <i>Ala</i> 1-NMe, <i>Val</i> 1-2
3	27.8	2.31 <i>m</i>	2, 4, 5		NMe, 2, 4, 5, <i>Thr</i> -NH, <i>Thr</i> -3
4	20.0	1.18 <i>d</i> 6.4	3	2, 3, 5	NMe, 2, 3, 5, <i>Ala</i> 1-NMe, <i>Val</i> 1-2, <i>Leu</i> -2, <i>Thr</i> -NH
5	19.9	0.98 <i>d</i> 6.9	3	2, 3, 4	NMe, 2, 3, <i>Val</i> 1-2, <i>Thr</i> -NH, <i>Thr</i> -Bz-3/7

^a ol = overlapping signals

Table T2. NMR data (in MeOH-*d*₄ at 23° C) for pteratide II (**2**).

Position	¹³ C [ppm]	¹ H [ppm, mult. ^a Hz]	COSY	HMBC	NOESY
<i>Thr</i>					
NH		7.85	2		
1	169.5				
2	53.0	5.22 <i>ol</i>	NH	1	4, <i>Leu</i> -NMe
3	72.5	5.20 <i>ol</i>	4	4, <i>Val</i> -1	4, <i>Leu</i> -NMe, <i>Ala</i> 1-NMe
4	16.9	1.34 <i>s</i>	3	2, 3	2, 3
Bz-1	169.4				
Bz-2	132.0				
Bz-3/7	127.1	7.77 <i>d</i> 7.6	Bz-4/6	Bz-1, Bz-3/7, Bz-5	Bz-4/6
Bz-4/6	128.6	7.43 <i>t</i> 7.6	Bz-3/7, Bz-5	Bz-2, Bz-3/7, Bz-4/6	Bz-3/7, Bz-5
Bz-5	132.1	7.51 <i>t</i> 7.4	Bz-4/6	Bz-3/7	Bz-4/6
<i>Leu</i>					
NMe	29.5	2.89 <i>s</i>		2, <i>Thr</i> -1	3a, 3b, <i>Thr</i> -2, <i>Thr</i> -2
1	169.7				
2	53.2	5.27 <i>ol</i>	3a, 3b	NMe, 1, 3	3b, 4, 6, <i>Ala</i> 1-NMe
3	37.0	1.29 <i>m</i>	2, 3b	1, 2, 4, 6	NMe, 3b, 6
		1.83 <i>m</i>	2, 3a, 4	2, 4, 5	NMe, 3a, 4, 6
4	24.7	1.43 <i>m</i>	3b, 5, 6		5
5	21.4	0.83 <i>ol</i>	4	3, 4	4
6	21.9	0.84 <i>ol</i>	4	5	2, 3a, 3b, 4- <i>MePro</i> -2
<i>Ala</i> 1					
NMe	29.0	2.54 <i>s</i>		2, <i>Leu</i> -1	3, 4- <i>MePro</i> -4Me, <i>Val</i> -4, <i>Leu</i> -2
1	168.4				
2	51.7	5.33 <i>q</i> 6.3	3	NMe, 1, 3, <i>Leu</i> -1	3, 4- <i>MePro</i> -5a, 4- <i>MePro</i> -5b
3	12.9	1.15 <i>d</i> 6.1	2	1, 2	NMe, 2, <i>Phe</i> -5/9
<i>4-MePro</i>					
1	173.2				
2	55.7	5.24 <i>ol</i>	3a, 3b		3a, 4-Me, <i>Leu</i> -6, <i>Ala</i> 2-2
3	35.3	1.81 <i>m</i>	2, 3b, 4	5	2, 3b, 4-Me
		1.88 <i>m</i>	2, 3a, 4	1	3a, 4
4	33.2	2.53 <i>m</i>	4-Me		3b, 4-Me, 5b
5	53.5	2.95 <i>m</i>	4, 5b	3, 4, 4-Me	4-Me, 5b, <i>Ala</i> 1-2
		3.72 <i>dd</i> 10.1, 6.1	4, 5a	3, 4, 4-Me	4, 5a, <i>Ala</i> 1-2
4-Me	16.9	0.97 <i>d</i> 6.7	4	3, 4, 5	2, 3a, 4, 5a
<i>Ala</i> 2					
NMe	28.2	2.32 <i>s</i>		2, 4- <i>MePro</i> -1	3, <i>Phe</i> -5/9
1	171.8				
2	55.9	4.91 <i>ol</i>	3	NMe, 1, 3, 4- <i>MePro</i> -1	3, 4- <i>MePro</i> -2, <i>Phe</i> -NH
3	13.5	1.22 <i>d</i> 6.9	2	1, 2	NMe, 2, <i>Ile</i> -5
<i>Phe</i>					
NH		9.31 <i>d</i> 7.0	2	<i>Ala</i> 2-1	3b, 5/9, <i>Ala</i> 2-2, 4- <i>MePro</i> -2
1	172.8				
2	54.7	4.53 <i>ddd</i> 11.5, 7.0, <2	NH, 3a, 3b		5/9, <i>Ile</i> -NMe
3	34.0	3.00 <i>m</i>	2, 3b	4, 5	2, 3b, 5/9
		3.29 <i>ol</i>	3, 3a	2, 4, 5	NH, 3a, 5/9
4	138.5				
5/9	128.8	7.36 <i>d</i> 7.4	6/8	3, 5/9, 7	NH, 2, 3a, 3b, 6/8, <i>Ala</i> 1-3, <i>Ala</i> 2-NMe, <i>Ile</i> -NMe
6/8	128.2	7.16 <i>t</i> 7.5	5/9, 7	4, 5/9, 6/8	5/9, 7
7	126.8	7.10 <i>t</i> 7.4	6/8		6/8

^aol = overlapping signals

Table T2. NMR data (in MeOH-*d*₄ at 23° C) for pteratide II (**2**).

Position	¹³ C [ppm]	¹ H [ppm, mult. ^a Hz]	COSY	HMBC	ROESY
<i>Ile</i>					
NMe	29.2	3.14 <i>s</i>		2, <i>Phe</i> -1	3, <i>Phe</i> -2, <i>Phe</i> -5/9
1	171.4				
2	56.2	5.14 <i>d</i> 10.9	3	NMe, 1, 3, 4, 5, <i>Phe</i> -1	5, <i>Val</i> -2, <i>Val</i> -5
3	33.2	2.17 <i>m</i>	2, 3-Me, 4b		NMe, 3-Me, 4
3-Me	18.8	0.77 <i>ol</i>	3	2, 3, 4	3
4	23.9	0.93 <i>ol</i>	4b, 5		4b
		1.43 <i>m</i>	3, 4a, 5	2, 6	4a, 5
5	15.0	0.78 <i>ol</i>	4a, 4b	3, 4	2, 4b, <i>Ala</i> 2-3
<i>Val</i>					
NMe	29.0	2.65 <i>s</i>		2, <i>Ile</i> -1	
1	168.8				
2	66.5	4.87 <i>ol</i>	3	NMe, 1, 3, 4, <i>Ile</i> -1	4, 5, <i>Ile</i> -2
3	27.0	2.42 <i>m</i>	2, 4, 5		4, 5
4	19.6	1.07 <i>d</i> 6.3	3	2, 3, 5	2, 3, 5, <i>Ala</i> 1-NMe
5	19.1	0.88 <i>d</i> 6.7	3	2, 3, 4	2, 3, 4, <i>Ile</i> -2

^a ol = overlapping signals

Table T3. NMR data (in MeOH-*d*₄ at 23° C) for pteratide III (**3**)

Position	¹³ C [ppm]	¹ H [ppm, mult. ^a Hz]	COSY	HMBC
<i>Thr</i>				
NMe	36.5	3.27 <i>s</i>		2, 3, Bz-1
1	172.7			
2	61.8	5.74 <i>bs</i>		1, 2, 3, 4, Bz-1
3	68.5	5.68 <i>q</i> 7.0	4	1, 2, 4, <i>Val3</i> -1
4	16.1	0.58 <i>d</i> 7.0	3	2, 3
Bz-1	174.4			
Bz-2	135.2			
Bz-3/7	128.3	7.47 <i>ol</i>		Bz-1, Bz-5
Bz-4/6	128.4	7.50 <i>ol</i>		Bz-2, Bz-3/7
Bz-5	131.2	7.50 <i>ol</i>		
<i>Phe</i>				
NMe	30.7	3.04 <i>s</i>		2, <i>Thr</i> -1
1	170.6			
2	63.3	5.05 <i>dd</i> 9.6, 4.5	3a, 3b	NMe, 1, 3, 4, <i>Thr</i> -1
3	35.1	3.13 <i>ol</i>	2, 3b	1, 2, 4, 5/9
		3.68 <i>dd</i> 15.0, 4.4	2, 3a	1, 2, 4, 5/9
4	137.8			
5/9	130.0	7.35 <i>ol</i>		3, 5/9, 7
6/8	128.9	7.31 <i>ol</i>	7	4, 5/9, 6/8
7	127.2	7.25 <i>m</i>	6/8	5/9
<i>Val1</i>				
NH		8.41 <i>d</i> 7.1	2	
1	174.2			
2	64.1	3.74 <i>m</i>	NH, 3	1, 3, 5, <i>Phe</i> -1
3	29.5	2.29 <i>m</i>	2, 4, 5	2, 5
4	18.5	1.00 <i>d</i> 6.9	3	2, 3, 5
5	19.4	1.09 <i>d</i> 6.7	3	2, 3, 4
<i>Val2</i>				
NH		7.66 <i>d</i> 9.7	2	
1	173.7			
2	54.1	4.51 <i>dd</i> 9.7, 6.5	NH, 3	1, 3, 4, 5, <i>Val1</i> -1
3	29.7	1.53 <i>m</i>	2, 4, 5	2, 4, 5
4	16.1	0.16 <i>d</i> 6.8	3	2, 3, 5
5	18.1	0.63 <i>d</i> 6.9	3	2, 3, 4
<i>Leu</i>				
NMe	30.0	3.11 <i>s</i>		2, <i>Val2</i> -1
1	174.1			
2	50.5	5.48 <i>dd</i> 12.1, 3.9	3a, 3b	NMe, 1, 3, 4, <i>Val2</i> -1
3	37.1	1.34 <i>ddd</i> 14.8, 10.5, 3.6	2, 3b, 4	1, 4, 5, 6
		2.02 <i>ddd</i> 14.8, 12.1, 3.4	2, 3a, 4	1, 2, 4, 5, 6
4	25.1	1.59 <i>m</i>	3a, 3b, 5, 6	
5	22.5	1.03 <i>ol</i>	4	3, 4, 6
6	21.3	1.07 <i>ol</i>	4	3, 4, 5
<i>Val3</i>				
NMe	29.5	2.98 <i>s</i>		2, <i>Leu</i> -1
1	170.2			
2	65.4	4.39 <i>d</i> 9.0	3	NMe, 1, 3, 4, <i>Leu</i> -1
3	30.1	2.45 <i>m</i>	2, 4, 5	2
4	19.7	1.05 <i>ol</i>	3	2, 3, 5
5	19.4	1.13 <i>d</i> 6.9	3	2, 3, 4

^aol = overlapping signals

Table T4. NMR data (in CDCl₃ at 23° C) for pteratide IV (**4**).

Position	¹³ C [ppm]	¹ H [ppm, mult. ^a Hz]	COSY	HMBC	ROESY ^b
<i>Val1</i>					
NMe	32.3	2.74 <i>s</i>		2, Bz-1	
1	170.9				
2	58.6	5.28 <i>d</i> 10.7	2	NMe, 1, 3, Bz-1	<i>Ile</i> -NMe
3	26.9	2.21 <i>m</i>	1, 4, 5	2	
4	19.5	0.77 <i>d</i> 7.0	3	2, 3, 5	
5	17.5	0.95 <i>ol</i>	3	2, 3, 4	
Bz-1	171.5				
Bz-2	135.6				
Bz-3/7	126.3	7.27 <i>ol</i>		Bz-1	
Bz-4/6	128.5	7.42 <i>ol</i>			
Bz-5	129.9	7.33 <i>ol</i>			
<i>Ile</i>					
NMe	30.3	3.09 <i>s</i>		2, <i>Val1</i> -1	<i>Val1</i> -2
1	169.6				
2	60.4	4.45 <i>d</i> 11.4	3	NMe, 1, 3, 3-Me, 4, <i>Val1</i> -1	
3	30.9	2.20 <i>m</i>	2, 3-Me, 4		
3-Me	16.1	0.70 <i>d</i> 6.5	3	2, 3, 4	
4	24.1	1.32 <i>ol</i>	3		
5	9.8	0.84 <i>t</i> 7.1	4		
<i>Thr</i>					
NH		7.15 <i>ol</i>	2	2, <i>Ile</i> -1	
1	168.8				
2	54.85	4.46 <i>d</i> 10.2	NH	1, 4	
3	71.6	5.71 <i>q</i> 7.1	4	2, 4, <i>Val3</i> -1	
4	16.0	0.93 <i>ol</i>	3	2, 3	
<i>Phe</i>					
NMe	31.8	2.82 <i>s</i>		2, <i>Thr</i> -1	
1	168.52				
2	62.8	4.63 <i>dd</i> 11.5, 3.9	3a, 3b	NMe, 1, 3, 4, <i>Thr</i> -1	
3	34.0	2.85 <i>ol</i>	2		
		3.62 <i>dd</i> 14.8, 3.7	2	2, 4, 5/9	
4	136.9				
5/9	128.8	7.28 <i>ol</i>		3	
6/8	128.7	7.30 <i>ol</i>			
7	127.1	7.30 <i>ol</i>			
<i>Val2</i>					
NH		7.15 <i>ol</i>	2	1, 2, <i>Phe</i> -1	
1	172.6				
2	54.3	4.88 <i>dd</i> 8.7, 2.6	NH, 3	1, 3, 4, 5, <i>Phe</i> -1	<i>Ala1</i> -NMe
3	29.7	2.26 <i>m</i>	2, 4, 5		
4	20.2	1.02 <i>d</i> 6.9	3	2, 3, 5	
5	15.8	0.66 <i>d</i> 6.5	3	2, 3, 4	
<i>Ala1</i>					
NMe	31.3	3.27 <i>s</i>		2, <i>Val2</i> -1	<i>Val2</i> -2
1	173.4				
2	49.8	6.41 <i>q</i> 7.2	3	NMe, 1, 3	<i>Ala2</i> -2, <i>Val3</i> -NH
3	15.0	1.29 <i>d</i> 7.3	2	1, 2	

^a ol = overlapping signals^b only interresidual correlations shown

Table T4. NMR data (in CDCl₃ at 23° C) for pteratide IV (**4**).

Position	¹³ C [ppm]	¹ H [ppm, mult. ^a Hz]	COSY	HMBC	ROESY ^b
<i>Ala2</i>					
NMe	28.7	2.72 <i>s</i>		2, <i>Ala1</i> -1	
1	169.2				
2	54.9	5.52 <i>q</i> 6.7	3	NMe, 1, 3, <i>Ala1</i> -1	<i>Ala1</i> -2, <i>Val3</i> -NH
3	14.7	1.36 <i>d</i> 6.8	2	1	
<i>Val3</i>					
NH		7.52 <i>d</i> 10.5	2	2, <i>Ala2</i> -CO	<i>Ala1</i> -2, <i>Ala2</i> -2
1	168.46				
2	58.2	4.57 <i>dd</i> 10.5, 6.6	NH, 3	1, 3, 4, 5, <i>Ala2</i> -CO	
3	32.3	1.89 <i>m</i>	2, 4, 5	2, 4, 5	
4	18.1	0.77 <i>ol</i>	4	3, 5	
5	19.4	0.91 <i>ol</i>	4	3, 4	

^a ol = overlapping signals^b only interresidual correlations shown

S1: ^1H NMR spectrum of pteratide I (**1**) in CDCl_3 .

S2: ^{13}C NMR spectrum of pteratide I (**1**) in CDCl_3 .

S3: COSY spectrum of pteratide I (**1**) in CDCl₃.

S4: TOCSY spectrum of pteratide I (**1**) in CDCl₃.

S14

S5: NOESY spectrum of pteratide I (**1**) in CDCl₃.

S15

1

S6: HSQC-DEPT spectrum of pteratide I (**1**) in CDCl₃.

S8: IMPRESS spectrum of pteratide I (**1**) in CDCl₃.

S9: ^1H NMR spectrum of pteratide II (**2**) in $\text{MeOH-}d_4$.

S19

S10: ^{13}C NMR spectrum of pteratide II (**2**) in $\text{MeOH-}d_4$.

S20

S11: COSY spectrum of pteratide II (**2**) in MeOH- d_4 .

S21

S12: TOCSY spectrum of pteratide II (**2**) in MeOH- d_4 .

S22

S13: NOESY spectrum of pteratide II (**2**) in MeOH- d_4 .

S23

S14: HSQC-DEPT spectrum of pteratide II (**2**) in MeOH- d_4 .

S19: TOCSY spectrum of pteratide III (**3**) in MeOH- d_4 .

S29

S22: ^1H NMR spectrum of pteratide IV (**4**) in CDCl_3 .

S32

S25: TOCSY spectrum of pteratide IV (**4**) in CDCl_3 .

S35

S26: ROESY spectrum of pteratide IV (4) in CDCl₃.

S36

S29: IMPRESS spectrum of pteratide IV (**4**) in CDCl_3 .

S30: ESI MS/MS data for pteratide I methyl ester.

Fragmentation of sodiated methyl ester ions of pteratide I (m/z 1041.7).

S31: ESI MS/MS data for pteratide II methyl ester.

Fragmentation of sodiated methyl ester ions of pteratide II (m/z 1055.7).

Table T5. HPLC analysis of FDAA derivatized acid hydrolyzates of pteratide I-IV (1-4).

amino acid	<i>t_R</i> of standards (min)			1	2	3	4
	eluent A ^a	eluent B ^b	eluent C ^c				
L-valine	10.32					*	*
D-valine	15.02						
L-threonine		8.87		*	*		*
D-threonine		12.85					
L- <i>allo</i> -threonine		10.16					
D- <i>allo</i> -threonine		10.88					
L-phenylalanine	15.72			*	*		
D-phenylalanine	20.88						
<i>N</i> -methyl-L-alanine		15.43		*	*		*
<i>N</i> -methyl-D-alanine		14.96					
<i>N</i> -methyl-L-valine	14.32			*	*	*	*
<i>N</i> -methyl-D-valine	17.83						
<i>N</i> -methyl-L-leucine	18.44			*	*	*	
<i>N</i> -methyl-D-leucine	21.27						
<i>N</i> -methyl-L-isoleucine	19.37				*		*
<i>N</i> -methyl-D-isoleucine	24.22						
<i>N</i> -methyl-L- <i>allo</i> -isoleucine	19.88						
<i>N</i> -methyl-D- <i>allo</i> -isoleucine	22.55						
<i>N</i> -methyl-L-threonine		9.91				*	
<i>N</i> -methyl-D-threonine		10.59					
<i>N</i> -methyl-L- <i>allo</i> -threonine		15.37					
<i>N</i> -methyl-D- <i>allo</i> -threonine		15.98					
<i>N</i> -methyl-L-phenylalanine	15.95					*	*
<i>N</i> -methyl-D-phenylalanine	16.70						
<i>trans</i> -4-methyl-L-proline		18.26	19.18	*	*		
<i>cis</i> -4-methyl-L-proline		16.62	17.85				
<i>trans</i> -4-methyl-D-proline		19.25	21.31				
<i>cis</i> -4-methyl-D-proline		18.48	20.67				

^aEluent A (solvents: A: water + 0.05 % TFA, B: MeCN; linear gradient: 0 min 35 % B, 30 min 45 % B; 25°C; 1 mL min⁻¹).

^bEluent B (solvents: A: water + 0.05 % TFA, B: MeOH; linear gradient: 0 min 45 % B, 30 min 65 % B; 24°C; 1 mL min⁻¹).

^cEluent C (solvents: A: water + 0.05 % HCOOH, B: MeOH; linear gradient: 0 min 45 % B, 30 min 65 % B; 24°C; 1 mL min⁻¹).