SUPPORTING INFORMATION

A Family of Macrocyclic Antibiotics with a Mixed Peptide-Peptoid ß-Hairpin Backbone Conformation

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Included here are tables giving:

1) ^{1}H-NMR (600 MHz) Chemical shifts for mimetic **6**.
2) ^3J (HN,H-C(α) Coupling constants for mimetic **6**
3) Upper distance restraints derived from integration of ROESY cross-peak volumes for the mimetic **6**.
4) Observed backbone torsion angles φ and ψ with standard deviation found in 15 NMR structures of the mimetic **6**, as shown in Fig. 1.

As well as CD spectra for the mimetics **5**, **6**, and **7**.

Table 1: ^{1}H-NMR (600 MHz) Chemical shifts for **6** in H_2O/D_2O 9:1, pH 5.0, 300 K.

	Chemical Shift (ppm)[a]			
Residue	NH	H-C(α)	H-C(β)	Others
Leu[1]	7.86	4.39	1.47,1.84	CH(γ) 1.60; CH_3(δ) 0.87, 0.96
Arg[2]	8.43	4.70	1.72,1.72[b]	CH_2(γ) 1.47, 1.61; CH_2(δ) 3.14, 3.14; NH(ε) 7.13; NH_2(η)[c] -, -
Leu[3]	8.50	4.63	0.90, 1.34	CH(γ) 1.34; CH_3(δ) 0.82, 0.85
Lys[4]	8.32	5.12	1.64, 1.82	CH_2(γ) 1.31, 1.31; CH_2(δ) 1.64, 1.64; CH_2(ε) 2.95, 2.95; NH_3^+(ζ)[c] -
Lys[5]	8.99	5.05	1.91, 2.02	CH_2(γ) 1.42, 1.51; CH_2(δ) 1.64, 1.64; CH_2(ε) 2.84, 2.84; NH_3^+(ζ)[c] -
NBG[6]	-	3.75, 4.35	-	CH_2(Nβ) 3.58, 3.70; CH_2(Nγ) 1.75, 1.78; CH_2(Nδ) -;

				CH_2(Nε) 3.09, 3.09
Arg[7]	8.41	4.20	1.44, 1.60	CH_2(γ) 1.03, 1.23; CH_2(δ) 2.97, 2.97; NH(ε) 6.95; NH_2(η)[c] -, -
Trp[8]	8.08	4.85	3.28, 3.39	H(δ^1) 7.30; H(ε^3) 7.75; H(ζ^3) 7.08; H(η^2) 7.19; H(ζ^2) 7.47; NH(ε^1) 10.10
Lys[9]	8.30	5.04	1.63, 1.73	CH_2(γ) 1.30, 1.43; CH_2(δ) 1.63, 1.63; CH_2(ε) 2.93, 2.93; NH_3^+(ζ)[c] -
Tyr[10]	8.69	4.78	2.82, 2.82[b]	H(δ) 6.84, 6.84; H(ε) 6.59, 6.59
Arg[11]	8.53	5.12	1.72, 1.85	CH_2(γ) 1.50, 1.64; CH_2(δ) 3.16, 3.16; NH(ε) 7.13; NH_2(η) [c]-, -
Val[12]	8.35	4.51	2.00	CH_3(γ) 0.95, 0.95
DPro[13]	-	w	1.93, 2.32	CH_2(γ) 2.05, 2.16; CH_2(δ) 3.53, 3.91
Pro[14]	-	4.50	2.08, 2.28	CH_2(γ) 1.94, 2.09; CH_2(δ) 3.75, 4.01

[a] Chemical shifts are measured relative to internal TSP [sodium(trimethylsilyl)-d_4-propionate].

[b] Stereospecific assignments are not available.

[c] Not determined due to overlapping resonances in the range: 7.75-7.65 and 7.11-6.96 ppm

Table 2: ^3J (HN,H-C(α)) Coupling constants.

Residue	^3J(α,NH) [Hz] [a]
1 LEU	8.2
2 ARG	9.5
3 LEU	9.5
4 LYS	8.9
5 LYS	8.9
7 ARG	8.3
8 TRP	8.7
9 LYS	9.5
10 TYR	8.0
11 ARG	9.0
12 VAL	9.6

[a] Measured in 1D and/or COSY spectra.

Table 3. Upper distance restraints derived from integration of ROESY cross-peak volumes for the mimetic **6**. These restraints were used to calculate the structures shown in Fig. 1 using DYANA.

Residue	atom	residue	atom	distance (Å)
1 LEU	HN	1 LEU	HB2	2.93
1 LEU	HN	1 LEU	HB3	3.58
1 LEU	HN	1 LEU	HG	3.21
1 LEU	HN	1 LEU	QD1	6.53
1 LEU	HN	1 LEU	QD2	6.53
1 LEU	HN	12 VAL	HN	4.20
1 LEU	HN	14 PRO	HA	3.36
1 LEU	HN	14 PRO	QG	4.84
1 LEU	HN	14 PRO	QD	4.60
1 LEU	HA	1 LEU	HB2	3.02
1 LEU	HA	1 LEU	HB3	2.77
1 LEU	HA	1 LEU	HG	2.65
1 LEU	HA	1 LEU	QD1	5.13
1 LEU	HA	1 LEU	QD2	5.13
1 LEU	HA	1 LEU	QQD	4.23
1 LEU	HA	2 ARG+	HN	2.40
1 LEU	HA	14 PRO	QB	4.71
1 LEU	HB2	12 VAL	HN	4.26
1 LEU	HG	14 PRO	QD	5.34
2 ARG+	HN	2 ARG+	HG2	4.20
2 ARG+	HN	2 ARG+	HG3	4.20
2 ARG+	HA	2 ARG+	HG2	3.61
2 ARG+	HA	2 ARG+	HG3	3.61
2 ARG+	HA	2 ARG+	QG	3.34
2 ARG+	HA	2 ARG+	QD	4.58
2 ARG+	HA	3 LEU	HN	2.46
2 ARG+	HA	11 ARG+	HA	2.65
3 LEU	HN	3 LEU	HB2	3.45
3 LEU	HN	3 LEU	HB3	3.45
3 LEU	HN	3 LEU	QB	3.17
3 LEU	HN	10 TYR	HN	4.54
3 LEU	HA	3 LEU	HB2	2.80
3 LEU	HA	3 LEU	HB3	2.80
3 LEU	HA	3 LEU	QB	2.55
3 LEU	HA	3 LEU	QD1	6.22
3 LEU	HA	3 LEU	QD2	6.22
3 LEU	HA	4 LYS+	HN	2.49
3 LEU	QB	4 LYS+	HN	3.93
3 LEU	QB	10 TYR	QE	8.14
3 LEU	QQD	10 TYR	QD	9.93
3 LEU	QQD	10 TYR	QE	9.24

3 LEU	QQD	12 VAL	HN	7.26
4 LYS+	HN	4 LYS+	HB2	3.36
4 LYS+	HN	4 LYS+	HB3	3.36
4 LYS+	HN	4 LYS+	QB	3.04
4 LYS+	HN	4 LYS+	QE	6.38
4 LYS+	HA	4 LYS+	HB2	2.87
4 LYS+	HA	4 LYS+	HB3	2.87
4 LYS+	HA	4 LYS+	QB	2.66
4 LYS+	HA	5 LYS+	HN	2.56
4 LYS+	HA	9 LYS+	HA	2.71
4 LYS+	HA	10 TYR	QD	6.83
4 LYS+	HA	10 TYR	QE	7.63
4 LYS+	QB	5 LYS+	HN	5.11
4 LYS+	QB	10 TYR	QE	8.51
4 LYS+	QG	5 LYS+	HN	6.38
5 LYS+	HN	5 LYS+	HB2	3.70
5 LYS+	HN	5 LYS+	HB3	3.67
5 LYS+	HN	8 TRP	HN	4.54
5 LYS+	HN	10 TYR	QD	7.64
5 LYS+	HN	10 TYR	QE	7.63
5 LYS+	HA	5 LYS+	HB2	2.83
5 LYS+	HA	5 LYS+	HB3	2.96
5 LYS+	HA	5 LYS+	HG2	3.55
5 LYS+	HA	5 LYS+	HG3	3.55
5 LYS+	HA	5 LYS+	QG	3.31
5 LYS+	HA	6 NBG	HNB1	2.80
5 LYS+	HA	6 NBG	HNB2	2.80
5 LYS+	HA	6 NBG	QNB	2.46
5 LYS+	HA	6 NBG	QNE	6.39
5 LYS+	HA	10 TYR	QE	7.63
5 LYS+	HB2	5 LYS+	QE	6.38
5 LYS+	HB2	8 TRP	HE3	5.38
5 LYS+	HB2	10 TYR	QD	7.64
5 LYS+	HB2	10 TYR	QE	6.21
5 LYS+	HB3	5 LYS+	QE	6.38
5 LYS+	HB3	8 TRP	HE3	4.76
5 LYS+	HB3	10 TYR	QD	7.64
5 LYS+	HB3	10 TYR	QE	7.07
5 LYS+	QE	8 TRP	HE1	6.38
5 LYS+	QE	10 TYR	QE	8.51
6 NBG	HNB1	6 NBG	QNE	6.39
6 NBG	HNB2	6 NBG	QNE	6.39
6 NBG	QNB	6 NBG	HA1	3.80
6 NBG	QNG	6 NBG	HA1	4.65
6 NBG	HA2	7 ARG+	HN	2.74
6 NBG	HA2	8 TRP	HN	2.93

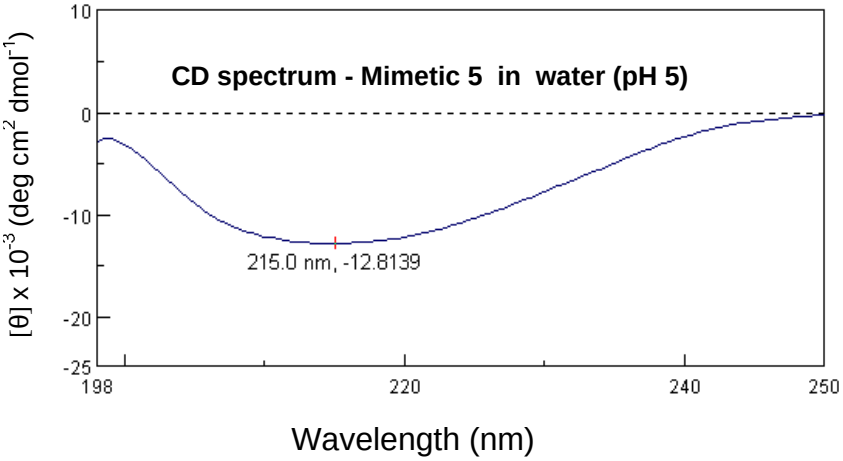
7 ARG+	HN	7 ARG+	HB2	3.92
7 ARG+	HN	7 ARG+	HB3	3.92
7 ARG+	HN	7 ARG+	QB	3.62
7 ARG+	HN	7 ARG+	HG2	4.79
7 ARG+	HN	7 ARG+	HG3	4.79
7 ARG+	HN	7 ARG+	QG	4.49
7 ARG+	HN	8 TRP	HN	3.76
7 ARG+	HA	7 ARG+	HB2	2.83
7 ARG+	HA	7 ARG+	HB3	2.83
7 ARG+	HA	7 ARG+	QB	2.57
7 ARG+	HA	7 ARG+	QG	3.77
7 ARG+	HA	7 ARG+	QD	5.23
7 ARG+	HA	8 TRP	HN	3.36
7 ARG+	QD	8 TRP	HZ2	6.38
8 TRP	HN	8 TRP	HB2	3.02
8 TRP	HN	8 TRP	HB3	3.39
8 TRP	HN	8 TRP	HD1	5.50
8 TRP	HN	8 TRP	HE3	5.50
8 TRP	HA	8 TRP	HD1	3.70
8 TRP	HA	8 TRP	HE3	3.52
8 TRP	HA	9 LYS+	HN	2.40
8 TRP	HB2	8 TRP	HD1	3.58
8 TRP	HB2	8 TRP	HE3	4.01
8 TRP	HB2	10 TYR	QE	7.48
8 TRP	HB3	8 TRP	HE3	3.76
8 TRP	HB3	9 LYS+	HN	3.73
8 TRP	HB3	10 TYR	QD	7.64
8 TRP	HB3	10 TYR	QE	7.63
9 LYS+	HN	9 LYS+	HG2	4.51
9 LYS+	HN	9 LYS+	HG3	4.51
9 LYS+	HN	9 LYS+	QG	4.25
9 LYS+	HN	9 LYS+	QE	6.38
9 LYS+	HA	9 LYS+	QG	3.65
9 LYS+	HA	10 TYR	HN	2.52
9 LYS+	HA	10 TYR	QD	6.96
10 TYR	QB	11 ARG+	HN	4.45
10 TYR	QD	11 ARG+	HN	7.64
10 TYR	QD	12 VAL	QQG	9.30
10 TYR	QE	12 VAL	QQG	8.51
11 ARG+	HN	11 ARG+	HB2	3.61
11 ARG+	HN	11 ARG+	HB3	3.61
11 ARG+	HN	11 ARG+	QB	3.27
11 ARG+	HN	11 ARG+	HG2	5.16
11 ARG+	HN	11 ARG+	HG3	5.16
11 ARG+	HN	11 ARG+	QG	4.84
11 ARG+	HN	11 ARG+	QD	6.38

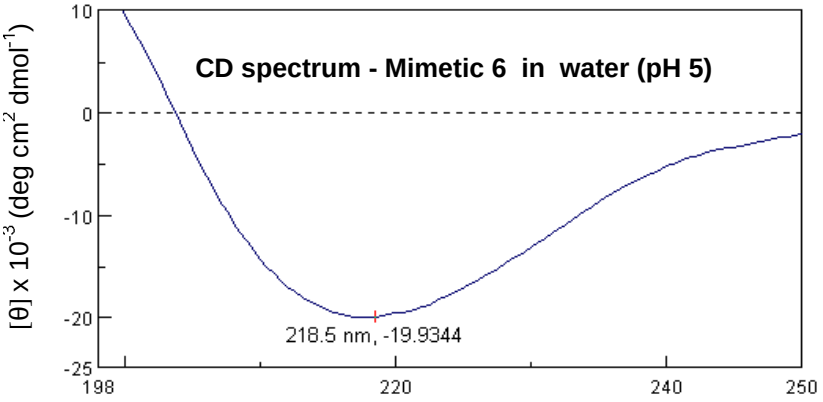
11 ARG+	HA	11 ARG+	QG	3.88
11 ARG+	HA	11 ARG+	QD	4.95
11 ARG+	HA	12 VAL	HN	2.43
11 ARG+	HB2	13 DPRO	HD3	6.76
11 ARG+	HB2	13 DPRO	HD2	6.76
11 ARG+	HB3	13 DPRO	HD3	6.76
11 ARG+	HB3	13 DPRO	HD2	6.76
11 ARG+	QB	13 DPRO	QD	5.35
11 ARG+	HG2	13 DPRO	HD3	6.45
11 ARG+	HG2	13 DPRO	HD2	6.45
11 ARG+	HG3	13 DPRO	HD3	6.45
11 ARG+	HG3	13 DPRO	HD2	6.45
11 ARG+	QG	13 DPRO	QD	5.29
12 VAL	HN	12 VAL	HB	3.11
12 VAL	HA	12 VAL	HB	2.99
12 VAL	HA	13 DPRO	HD3	2.62
12 VAL	HA	13 DPRO	HD2	2.62
12 VAL	HA	13 DPRO	QD	2.35

Table-4. Observed average backbone torsion angles φ and ψ with standard deviation found in 15 NMR structures of the mimetic **6**, as shown in Fig. 1.

1	LEU	PSI	129.1 +/- 42.2
2	ARG	PHI	-100.1 +/- 80.6
2	ARG	PSI	90.9 +/- 20.4
3	LEU	PHI	-98.5 +/- 10.8
3	LEU	PSI	150.1 +/- 17.9
4	LYS	PHI	-127.3 +/- 16.7
4	LYS	PSI	130.9 +/- 30.0
5	LYS	PHI	-135.3 +/- 41.7
5	LYS	PSI	89.9 +/- 13.3
6	NBG	PHI	25.7 +/- 16.0
6	NBG	PSI	-143.1 +/- 53.3
7	ARG	PHI	-39.4 +/- 51.2
7	ARG	PSI	-4.2 +/- 4.2
8	TRP	PHI	-119.6 +/- 9.8
8	TRP	PSI	148.3 +/- 19.1
9	LYS	PHI	-148.0 +/- 11.3
9	LYS	PSI	137.2 +/- 23.9
10	TYR	PHI	-147.3 +/- 18.5
10	TYR	PSI	151.9 +/- 75.7
11	ARG	PHI	-108.9 +/- 76.6
11	ARG	PSI	117.5 +/- 31.2
12	VAL	PHI	-131.7 +/- 13.4

12	VAL	PSI	111.5 +/-	16.2
13	DPRO	PHI	54.3 +/-	15.4
13	DPRO	PSI	-114.6 +/-	44.9
14	PRO	PHI	-59.7 +/-	24.4


CD spectrum - Mimetic 5 in water (pH 5)
[θ] x 10-3 (deg cm2 dmol-1)
10
0
-10
-20
-25
198
220
240
250
215.0 nm, -12.8139
Wavelength (nm)


CD spectrum - Mimetic 6 in water (pH 5)
[θ] x 10-3 (deg cm2 dmol-1)
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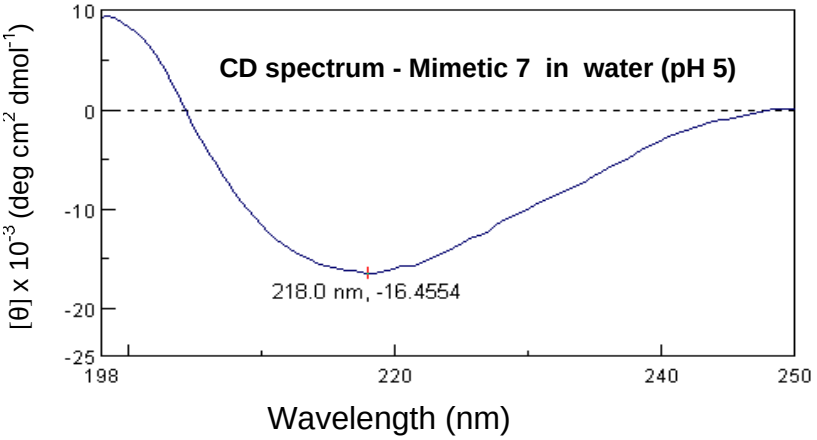
-10
-20
-25
198
220
240
250
218.5 nm, -19.9344
Wavelength (nm)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[θ] x 10-3 (deg cm2 dmol-1)
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-10
-20
-25
198
220
240
250
218.0 nm, -16.4554
Wavelength (nm)