Supporting Information

Solution Conformations of Mycothiol Bimane, 1-D-GlcNAc- β -(1 $\rightarrow$ 1)-D-*myo*-Ins and 1-D-GlcNAc- β -(1 $\rightarrow$ 1)-L-*myo*-Ins

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MSmB Roesy, 500 MHz, $t_m=110$ ms

HSQMBC Spectrum of MSmB

Expansion of anomeric region of HSQMBC Spectrum

$$^3J_{\text{H1}'\text{-H1}''} = 3.5 \text{ Hz}$$

$$\text{Diff} = ^3J_{\text{H1}'\text{-C1}''} = 3.5 \text{ Hz}$$

HSQMBC spectrum and expansion of anomeric region. A 7.0 Hz coupling for $\text{H1}'\text{-C1}''$ was observed in the HSQMBC spectrum. This is the sum of the homonuclear $^1J_{\text{HH}}$ and heteronuclear $^3J_{\text{CH}}$ coupling constants. The homonuclear coupling constant for $\text{H1}'$ (to $\text{H2}'$) is 3.5 Hz. Thus, the difference of 3.5 Hz yields the heteronuclear coupling constant.

Table 1. D-GI NMR assignments^a and distance correlations.

Residue		δ_C	δ_H	J (Hz)	NOE (Intensity ^b)
<i>N</i> -Acetyl-1- β -D-glucosamine	1	99.4	5.12	d 3.5	1' (s), 2' (m), 6' (m), 2 (m), 3 (m), 4 (w), 5 (w)
	2	54.3	3.96	dd 10, 3.5	1 (m), 4 (m)
	3	71.0	3.78	t 10	1 (m), 4 (m)
	4	70.4	3.48	t 10	1 (w), 2 (m), 3 (m), 5 (m)
	5	72.8	3.86	m	2' (w), 1 (w), 4 (m)
	6a	60.9	3.79	m	
	6b		3.88	m	
	HN		8.43	d 9	1 (m), CH ₃ (s)
	CO	176.7			
	CH ₃	22.0	2.04	s	
1-D- <i>myo</i> -Inositol	1'	79.4	3.58	dd 10, 3	1 (s), 2' (m), 6' (m)
	2'	72.4	4.19	t 3	1 (m), 5 (w), 1' (m), 3' (m), 4' (m), 5' (w), 6' (m)
	3'	71.4	3.52	dd 10, 3	2' (m), 4' (m), 5' (m)
	4'	72.4	3.62	t 10	2' (m), 3' (m)
	5'	74.5	3.28	t 10	2' (m), 3' (m)
	6'	72.4	3.76	t 10	1 (m), 1' (m), 2' (m)

^aReferenced to D₂O at 27 °C, pH 6.5. ^bThe letters s, m and w refer to strong, medium and weak intensities. See Experimental Section for distances used in structure calculations.

Table 2. L-GI NMR assignments^a and distance correlations.

Residue		δ_C	δ_H	J (Hz)	NOE (Intensity ^b)
<i>N</i> -Acetyl-1- β -D-glucosamine	1	96.9	4.99	d 3.5	1' (s), 2' (m), 6' (w), 2 (m), 3 (m)
	2	56.2	3.89	dd 10, 3.5	1 (m), 3 (m), 4 (m)
	3	73.5	3.78	t 10	2 (m), 4 (m)
	4	72.4	3.48	t 10	2 (m), 3 (m)
	5	74.6	3.9	m	1' (m), 6' (w)
	6a	63	3.75	m	
	6b		3.75	m	
	HN		8.09	d 9	1 (m), CH ₃ (s)
	CO	177.2			
	CH ₃	24.6	1.99	s	
1-L- <i>myo</i> -Inositol	1'	78.1	3.54	dd 10, 3	1 (s), 5 (m), 2' (m), 3' (m), 5' (m), 6' (m)
	2'	70.9	4.12	t 3	1 (m), 1' (m), 3' (m)
	3'	73.8	3.43	dd 10, 3	1' (m), 2' (m), 4' (m), 5' (m)
	4'	74.8	3.6	t 10	2' (m), 5' (m), 6' (m)
	5'	76.9	3.25	t 10	1' (m), 3' (m), 4' (m), 6' (m)
	6'	73.6	3.66	t 10	1 (m), 5 (w), 1' (m), 4' (m), 5' (m)

^aReferenced to D₂O at 27 °C, pH 6.5. ^bThe letters s, m and w refer to strong, medium and weak intensities. See Experimental Section for distances used in structure calculations.

Table 3. MSmB NMR assignments^a and distance correlations.

Residue	Atom Number	Atom Type	δ_C	δ_H	J (Hz)	NOE (Intensity ^b)
<i>N</i> -Acetyl-L-Cysteine	1	CO	172.2			
	2	C β	53.2	4.57	m	3a (s), 3b (s), 8a (vw), 8b (w), 5 (w), 9 (vw), 7 (m)
	3	C α	33.8	2.96	dd 14, 8.5	7 (m), 3b (s), 2 (s), 8b (w)
				3.14	dd 14, 4.5	7 (m), 3a (s), 2 (s), 8a (w), 8b (vw)
	4	CO	174.5			
	5	CH ₃	22.0	2.04	s	6'' (w), 2 (w)
Bimane	HN	HN		8.39	br d 4.5	2 (w), 5 (s)
	1	CO	162.6			
	2	C	113.8			
	3	C	148.3			
	4	C	150.0			
	5	C	111.8			
	6	CO	163.3			
	7	CH ₃	6.4	1.86	s	2 (m), 8a (w), 8b (w), 3a (m), 3b (m)
	8a	CH ₂	25.2	3.91	d 15	7 (w), 9 (w), 3b (vw), 2 (vw)
	8b	CH ₂		3.93	d 15	7 (w), 9 (w), 3a (w), 3b (w), 2 (w)
α -D-Glucosamine	9	CH ₃	11.4	2.44	s	2 (vw), 8a (w), 8b (w)
	10	CH ₃	5.9	1.78	s	
	1'	CH	99.4	5.12	d 3.5	1'' (s), 2'' (m), 6'' (m), 2' (s)
	2'	CH	54.3	3.96	dd 10, 3.5	1' (m), 4' (m)
	3'	CH	71.0	3.78	t 10	4' (m)
	4'	CH	70.4	3.48	t 10	2' (m), 3' (m), 5' (m)
	5'	CH	72.8	3.86	m	1'' (w), 2'' (s), 4' (m)
	6a'	CH ₂	60.9	3.79	m	
1- D- <i>myo</i> -Inositol	6b'	CH ₂		3.88	m	
	H'N	HN		8.21	d 9	2 (s), 1' (m)
	1''	CH	79.4	3.58	dd 10, 3	1' (s), 5' (w), 2'' (m)
	2''	CH	72.4	4.19	t 3	1' (m), 5' (s), 1'' (m), 3'' (m), 4'' (m)
	3''	CH	71.4	3.52	dd 10, 3	2'' (m)
	4''	CH	72.4	3.62	t 10	2'' (m), 5'' (m)
	5''	CH	74.5	3.28	t 10	4'' (m), 6'' (m)
	6''	CH	72.4	3.76	t 10	1' (m), 5'' (m), 5 (w)

^aReferenced to D₂O at 27 °C, pH 6.5. ^bThe letters s, m and w refer to strong, medium and weak intensities. See Experimental Section for distances used in structure calculations.