

TABLE S1. NMR resonance assignment for RPS of *S. oralis* MC2

Residue	H1	H2	H3	H4	H5	H6, H6'	NAc
	C1	C2	C3	C4	C5	C6	CH ₃
(A) GalNAc α	5.073 95.08	4.219 50.42	4.019 68.02	4.074 68.60	4.355 70.26	3.994, 4.053 65.08	2.058 22.79
(B) Rha β	4.849 101.06	4.203 68.02	3.661 78.24	3.432 71.07	3.443 72.73	1.350 17.40	
(C) Glu β	4.513 103.19	3.343 73.77	3.647 75.89	3.643 77.15	3.537 75.25	3.829, 3.944 61.35	
(D) Gal β	5.061 108.19	4.072 81.50	4.097 77.25	3.990 83.54	4.013 70.25	3.751, 4.058 71.81	
(E) GalNAc β	4.533 105.01	3.533 71.10	3.638 72.97	3.928 69.33	3.825 74.23	3.781, 3.900 67.77	
(F) GalNAc α	5.486 94.88	4.383 49.28	4.087 77.26	4.282 69.09	4.164 72.28	3.751, 3.784 61.72	2.058 22.79

TABLE S2. Inter-residual connectivities in polysaccharide from *S. oralis* MC2

NMR Experiment	Residue					
	(A) GalNAc α 1 \rightarrow	(B) Rha β 1 \rightarrow	(C) Glc β 1 \rightarrow	(D) Gal β 1 \rightarrow	(E) Gal β 1 \rightarrow	(F) GalNAc α 1 \rightarrow
NOESY (100 ms)	H1(A)-H3(B)	H1(B)-H4(C)	H1(C)-H6(D) H1(C)-H6'(D)	ND ^a	H1(E)-H3(F)	ND
HMBC	H1(A)-C3(B) C1(A)-H3(B)	H1(B)-C4(C) C1(B)-H4(C)	H1(C)-C6(D) C1(C)-H6(D)	H1(D)-C6(E) C1(D)-H6(E)	H1(E)-C3(F)	ND

^a Linkage not detected.