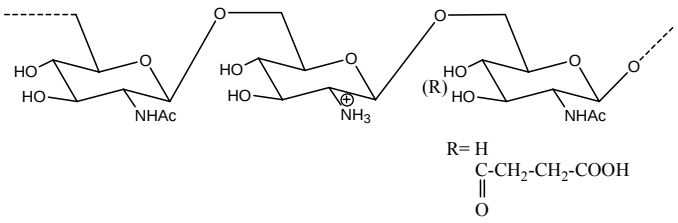
a)



b)

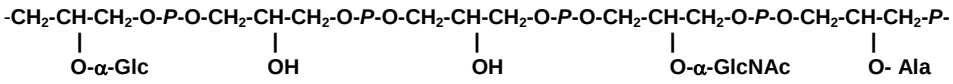


Figure S.1. The structures of (a) PNAG and (b) TA from *S. epidermidis* 5.

TA constituent	Position	^{1}H Shift / ppm	^{13}C Shift / ppm
α-Glc	1/1’	5.19	99.1
	2	3.55	72.8
	3/3’	3.78	74.3
	4	3.42	71.0
	5	3.92	73.3
	6	3.78	62.0
	6’	3.90	
α-GluNAc	1/1’	5.10	98.2
	2	3.95	55.0
	3/3’	3.82	72.3
	4	3.49	71.4
	5	3.95	73.3
	6	3.78	62.0
	6’	3.90	
	CH_3	2.10	23.5
Ala	1		171.3
	2	4.30	50.3
	3	1.64	16.7
Gro - Ala	2	5.39	75.5
	1/1’&3/3’	4.13	65.0
Gro - Glc	1/1’	4.04	65.9*
	3/3’	4.04	66.6*
	2	4.13	76.8
Gro - GluNAc	1/1’	4.04	65.9*
	3/3’	4.04	66.6*
	2	4.07	77.2
Gro - Free	1/1’	3.92	67.6
	3/3’	3.98	67.6
	2	4.06	70.8

Table S.1. The ^{1}H and ^{13}C chemical shifts of each extracellular TA substituent from *S. epidermidis* 5. Constituents beginning Gro denote that part of the glycerol phosphate backbone and the various substituents. * indicates can be interchanged inside residue. ^{1}H and ^{13}C chemical shifts of EC TA from *S. epidermidis* 5, as assigned by 2D homonuclear and heteronuclear correlation techniques on a Varian UnityINOVA 500 MHz NMR Spectrometer.

TA constituent	Position	^{1}H Shift / ppm	^{13}C Shift / ppm
α-Glc	1	5.178	100.43
	2	3.542	74.18
	3	3.764	75.67
	4	3.410	72.43
	5	3.933	74.59
	6	3.764	63.33
	6’	3.897	63.33
α-GluNAc	1	5.080	-
	2	3.939	56.23
	3	3.807	73.66
	4	3.483	72.72
	5	3.939	74.59
	6	3.764	63.33
	6’	3.897	63.33
	NAc: CH_3	2.054	25.02
Ala	2	4.27	51.53
	3	1.609	18.04
Gro - Ala	2	5.383	76.89
	1&3	4.091	66.37
Gro - Glc	1	4.044	66.99
	1’	3.975	66.99
	3	4.044	68.00
	3’	3.975	68.00
	2	4.119	78.07
Gro - GluNAc	1	4.044	66.99
	1’	3.975	66.99
	3	4.044	68.00
	3’	3.975	68.00
	2	4.060	78.44
Gro - Free	1&3	3.954	68.96
	1’&3’	3.888	68.96
	2	4.036	72.28
αGlc - ala	1	5.197	100.09
	2	3.558	73.98
	3	3.973	73.78
	4	3.410	72.43
	5	4.192	71.09
	6	4.437	-
	6’	4.643	-

Table S.2. Repeated ^{1}H and ^{13}C chemical shifts of each extracellular TA substituent used in SXS TOCSY resonance assignments. (-) denotes ^{13}C chemical shift cannot be elucidated as falls within the solvent suppression area of HSQC spectra. As above, constituents beginning Gro denote that part of the glycerol phosphate backbone and the various substituents. Tentative assignment of α-Glucose O-6 alanine also listed in the table, however its presence in *S. epidermidis* 5 has not previously been observed (11/E. Vinogradov, unpublished observations)

PNAG constituent	Position	^{1}H Shift / ppm	^{13}C Shift / ppm
β-GlcNAc	1	4.518	-
	2	3.710	58.13
	3	3.550	76.40
	4	3.401	72.72
	5	3.550	65.21
	6	4.168	71.21
	6’	3.710	71.21
	CH_3	2.058	25.01
β- $GlcNH_2$	1	4.542	-
	2	2.775	58.86
	3	3.495	72.71
	4	3.387	77.00
	5	3.589	72.31
	6	4.168	71.21
	6’	3.710	71.21

Table S.3. The ^{1}H and ^{13}C chemical shifts of each PNAG constituent. (-) denotes ^{13}C chemical shift cannot be elucidated as falls within the solvent suppression area of HSQC spectra.

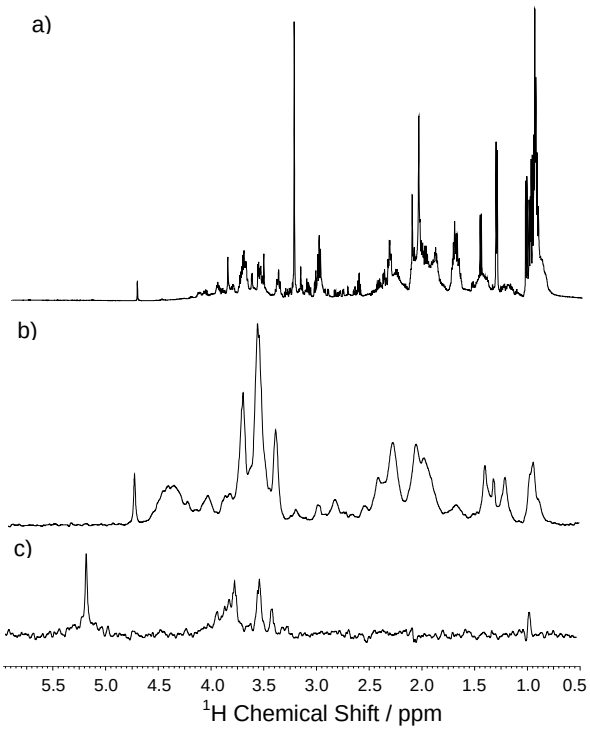


Figure S.2. a) A 1D ^{1}H spectrum, b) XS-TOCSY excitation at 4.5ppm and c) XS-TOCSY excitation at 5.2ppm of a crude, de-proteinated biofilm extract of the *S. epidermidis* strain RP62A in D_2O. Excitation at 4.5ppm gave ^{1}H resonances of note at 4.76, 3.71, 3.55 and 3.40ppm. Excitation at 5.2ppm gave ^{1}H resonances at 5.18, 3.98, 3.76, 3.53, 3.41ppm.

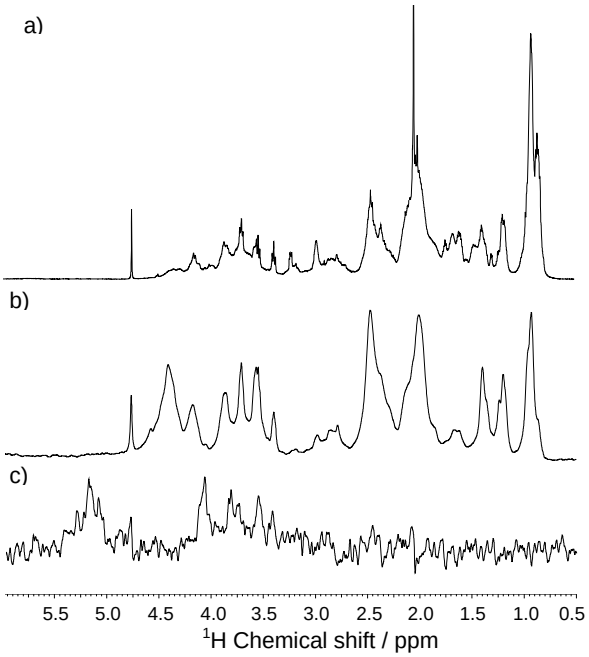


Figure S.3. a) A 1D ^{1}H spectrum, b) XS-TOCSY excitation at 4.5ppm and c) XS-TOCSY excitation at 5.2ppm of a crude, de-proteinated biofilm extract of the *S. epidermidis* strain 444 in D_2O. Excitation at 4.5ppm gave ^{1}H resonances of 4.76, 3.71, 3.55 and 3.40ppm. Excitation at 5.2ppm gave ^{1}H resonances of note at 5.28, 5.18, 4.06, 3.53, and 3.41ppm.

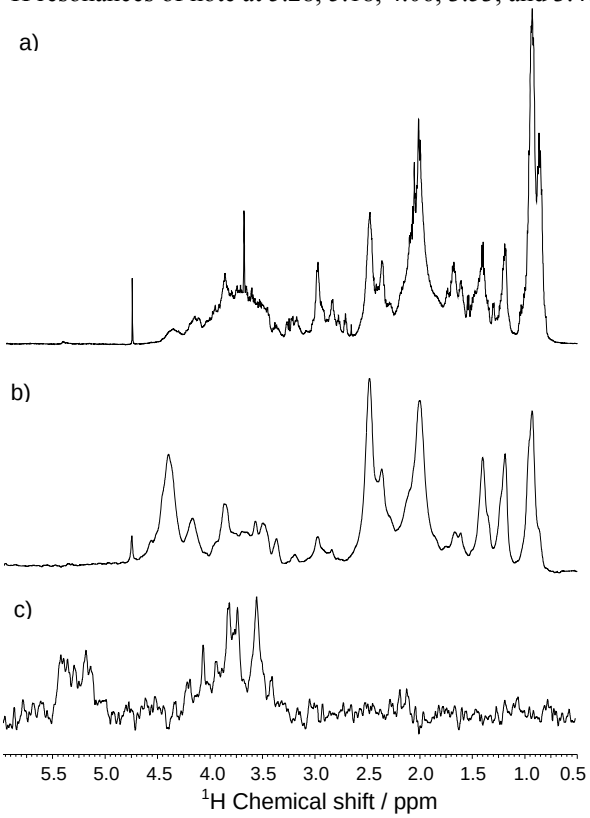


Figure S.4. a) A 1D ^{1}H spectrum, b) XS-TOCSY excitation at 4.5ppm and c) XS-TOCSY excitation at 5.2ppm of a crude, de-proteinated biofilm extract of the *S. epidermidis* strain 341 in D_2O. Excitation at 4.5ppm gave ^{1}H resonances of 4.76, 3.71, 3.55 3.40 and 1.61ppm. Excitation at 5.2ppm gave ^{1}H resonances of note at 5.18, 4.06, 3.98, 3.76, 3.53 and 3.41ppm.

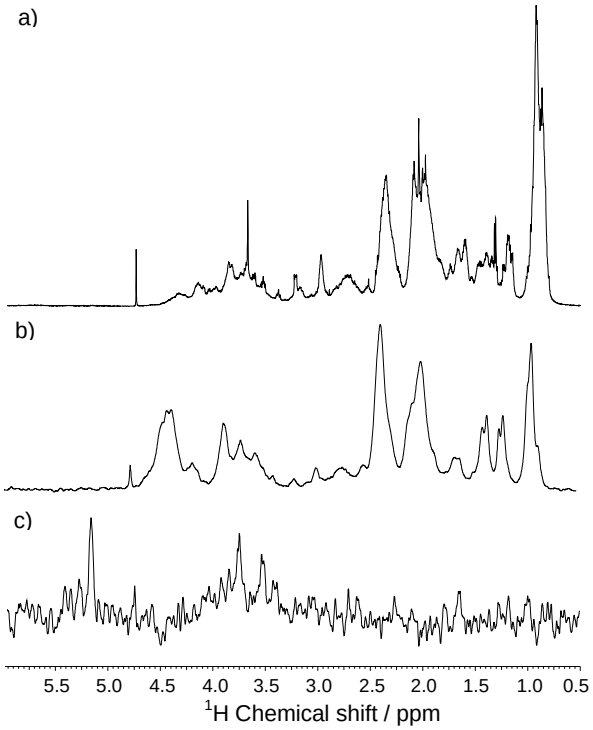


Figure S.5. a) A 1D ^{1}H spectrum, b) XS-TOCSY excitation at 4.5ppm and c) XS-TOCSY excitation at 5.2ppm crude (not de-proteinated) biofilm extract of the *S. epidermidis* strain 444 in D_2O. Excitation at 4.5ppm gave ^{1}H resonances of 4.76, 3.71, 3.55 and 3.40ppm. Excitation at 5.2ppm gave ^{1}H resonances of note at 5.18, 4.06, 3.98, 3.76, 3.58 and 3.41ppm.