S3: Chemical shift assignments (ppm) of ^{13}C and ^{1}H atoms in the five α-anomer hexosamines

Hexosamine	Assignment	^{13}C	^{1}H
GlcNAc	**C1-H1**	93.579	5.194
GlcNAc	**C2-H2**	56.788	3.868
GlcNAc	**C3-H3**	73.374	3.754
GlcNAc	**C4-H4**	72.771	3.478
GlcNAc	**C5-H5**	74.247	3.847
GlcNAc	**C6-H61**	63.262	3.836
GlcNAc	**C6-H62**	63.253	3.786
GlcNS	**C1-H1**	94.060	5.434
GlcNS	**C2-H2**	60.750	3.205
GlcNS	**C3-H3**	73.778	3.608
GlcNS	**C4-H4**	72.783	3.463
GlcNS	**C5-H5**	73.982	3.823
GlcNS	**C6-H61**	63.319	3.762
GlcNS	**C6-H62**	63.317	3.831
GlcNS6S	**C1-H1**	94.109	5.431
GlcNS6S	**C2-H2**	60.607	3.225
GlcNS6S	**C3-H3**	73.694	3.613
GlcNS6S	**C4-H4**	72.456	3.515
GlcNS6S	**C5-H5**	72.141	4.019
GlcNS6S	**C6-H61**	69.912	4.248
GlcNS6S	**C6-H62**	69.912	4.248
GlcNS6S3S	**C1-H1**	94.313	5.451
GlcNS6S3S	**C2-H2**	59.419	3.370
GlcNS6S3S	**C3-H3**	81.050	4.382
GlcNS6S3S	**C4-H4**	71.130	3.691
GlcNS6S3S	**C5-H5**	72.174	4.099
GlcNS6S3S	**C6-H61**	69.788	4.270
GlcNS6S3S	**C6-H62**	69.788	4.270
GlcNS3S	**C1-H1**	94.237	5.439
GlcNS3S	**C2-H2**	59.485	3.333
GlcNS3S	**C3-H3**	81.258	4.364
GlcNS3S	**C4-H4**	71.398	3.634
GlcNS3S	**C5-H5**	73.987	3.882
GlcNS3S	**C6-H61**	63.169	3.821
GlcNS3S	**C6-H62**	63.163	3.793

Data were recorded with a ^{1}H frequency of 600 MHz

Description of chemical shifts

The C1 chemical shift in the sulfonated hexosamines was downfield of the corresponding value in GlcNAc by ≈0.5 ppm. Sulfonation at the N-position caused a downfield shift at C2 in the range 2.6 to 3.9 ppm and C3 experienced the largest downfield shift due to 3-O-suolfonation, ≈8 ppm, in the two 3-O-suolfonated hexosamines GlcNS3S and and GlcNS6S3S. Carbon atoms C4 and C5 were shiffed upfield (0.3 to 2.1 ppm) in the di-sulfonated hexosamines relative to the corresponding values in unsulfonated GlcNAc. In monosulfonated GlcNS the values of the chemical shifts of carbon atoms C4 and C5 were marginally perturbed downfield and upfield by 0.01 and 0.3 ppm, respectively. The magnitude of the perturbation in pyranose ring proton chemical shifts due to sulfonation was smaller than for the carbon atoms. The largest changes were seen for protons H2 and H3. In the N-sulfonated hexosamines the H2 chemical shift was ≈0.5 ppm upfield of the corresponding value in GlcNAc. In the 3-O-sulfonated hexosamines the H3 proton chemical shift was ≈0.6 Hz downfield of the GlcNAc value.