




















Table S2. Annotations, experimental and theoretical masses, and accuracies of fragment ions included in Fig. 2, 4, 5, S6, S11, and S12. Fragment ions previously annotated by us are not included¹.

Proposed structure	Experimental mass	Theoretical mass	z	Accuracy (ppm)	Figure reference
+CO S	328.0345	328.0344	1	-0.3	2C
+CO +Ac S	370.0446	370.0450	1	1.1	2C
-CO ₂ S	396.0625	396.0606	1	-4.8	2C
+Ac S -H ₂ O	411.5855	411.58495	2	-1.3	4B
¹⁴ A S -H ₂ O	505.6012	505.60095	2	-0.5	4B
S	560.1845	560.1832	1	-2.3	4B
-CO -H ₂ O S	674.2158	674.2149	1	-1.3	4B
S	796.1461	796.1459	1	-0.3	4B
S	553.1088	553.1080	1	-1.4	4C
S S	640.1407	640.1400	1	-1.1	4C
EGS -CO ₂ -2H ₂ O	210.0887	210.0883	1	-1.9	4E
EEGS -CO ₂ -2H ₂ O	339.1313	339.1309	1	-1.2	4E
EEGS -CO ₂ -H ₂ O	357.142	357.1415	1	-1.4	4E
EEGS -H ₂ O	401.1318	401.1313	1	-1.2	4E
EEGS	437.1379	437.14125	2	7.7	4E
-CO ₂ EEGS	494.1574	494.1571	2	-0.6	4E
EEGS	713.2371	713.2370	1	-0.1	4E
-H ₂ O EEGS	857.2803	857.2792	1	-1.3	4E
EEGS	875.2907	875.2898	1	-1.0	4E
S S S	738.6541	738.65625	2	2.9	4F

SA -H ₂ O	157.0622	157.0618	1	-2.5	S10F
 SA	631.2216	631.2203	1	-2.1	S10F
-CO ₂ -H ₂ O	745.2521	745.2520	1	-0.1	S10H
 SA	807.2527	807.2524	1	-0.4	S10I
 GS	697.1615	697.1614	1	-0.1	S10J
 SA	711.1774	711.1771	1	-0.4	S10J
	355.0851	355.0849	2	-0.6	S11F
 S	851.2794	851.2786	1	-0.9	S10J
-CO ₂ -H ₂ O	965.3118	965.3103	1	-1.6	S10J
 S					
-CO ₂ -H ₂ O	731.2375	731.2363	1	-1.6	S10K
 S					
-CO ₂ -H ₂ O	1022.3348	1022.3317	1	-3.0	S10K
 GS					
 GS	1154.3395	1154.3376	1	-1.6	S10K
 SA					
-H ₂ O	789.2427	789.2418	1	-1.1	S10L
 SA					
-CO ₂	878.3282	878.3259	1	-2.6	S10L
 SA					
 SA	1010.3214	1010.3318	1	10.3	S10L
 SA					
 SA	1168.3544	1168.3533	1	-0.9	S10L
 SA					
EGS -CO ₂ -H ₂ O	228.0996	228.0989	1	-3.1	S11A
EGS -H ₂ O	272.089	272.0887	1	-1.1	S11A
 EGS	291.5931	291.5935	2	1.5	S11A
	584.1943	584.1944	1	0.2	S11A
 EGS	337.0776	337.0776	1	0.0	S11A
 EGS	728.2357	728.2366	1	1.2	S11A

^{14}A ◇ ●S ★ -H ₂ O	316.0456	316.0452	2	-1.3	S11C
+Ac ●S ★	595.119	595.1186	1	-0.7	S11C
◇ ●S ★	711.1296	711.1295	1	-0.1	S11C
◇ ●S ●S ★	798.1581	798.1615	1	4.3	S11C
E-H ₂ O	128.0356	128.0353	1	-2.3	S11D
EG -H ₂ O	185.0569	185.0567	1	-1.1	S11D
EEG -H ₂ O	314.0997	314.0993	1	-1.3	S11D
+Ac ●S ●S ★ EEGS	498.1252	498.12495	2	-0.5	S11D
★ SA	307.1147	307.1147	1	0.0	S11E
● ★ SA	469.1678	469.1675	1	-0.6	S11E
-CO ₂ ◇ ● ◇ ★ SA	517.6699	517.67005	2	0.3	S11E
-H ₂ O ● ● ★ SA	613.2095	613.2097	1	0.3	S11E
+Ac +CO ● ● ★ SA	701.2256	701.2258	1	0.3	S11E
◇ ● ◇ ★ SA	922.3057	922.3157	1	10.8	S11E
+Ac ●S ●S ★ SA	376.0903	376.0902	2	-0.3	S11F
◇ ●S ●S ★ SA	434.0957	434.09565	2	-0.1	S11F
+Ac -CO ₂ ●S ◇ ★ SA	499.643	499.643	2	0.0	S11F
◇ ●S	208.0138 417.0347	208.01355 417.0344	2 1	-1.2	S11G
◇ ●S ●S -H ₂ O	280.0349	280.03465	2	-0.9 -0.7	S11G
^{24}A ◇ ●S ●S ★	310.0456	310.04525	2	-1.1	S11G
-CO ₂ ^{14}A ◇ ●S ◇ ★ -H ₂ O	439.5982	439.598	2	-0.5	S11G
+Ac ●S ●S ★ S	682.1507	682.1506	1	-0.1	S11G
+Ac ●S ●S ★ GS	739.1721	739.1720	1	-0.1	S11H
◇ ●S ●S ★ GS	855.1846	855.1829	1	-2.0	S11H

Reference

- 1 Persson, A., Vorontsov, E., Larson, G. & Nilsson, J. Glycosaminoglycan Domain Mapping of Cellular Chondroitin/Dermatan Sulfates. *Sci Rep.* **10**, 3506, doi:10.1038/s41598-020-60526-0 (2020).