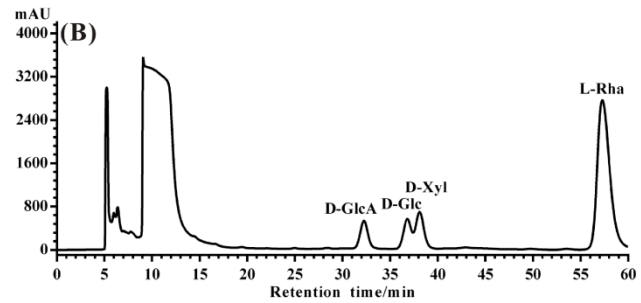
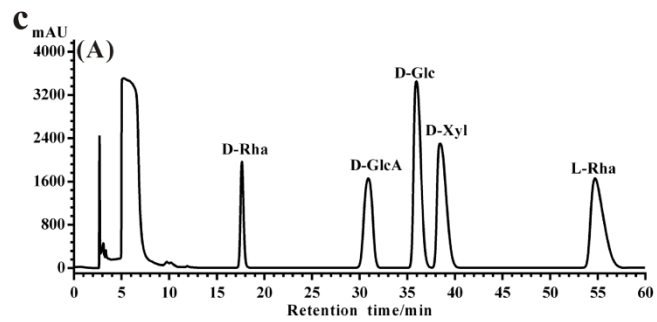
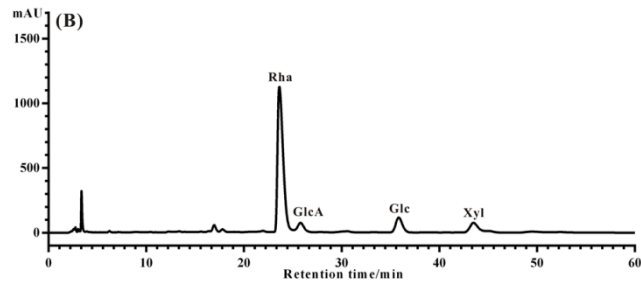
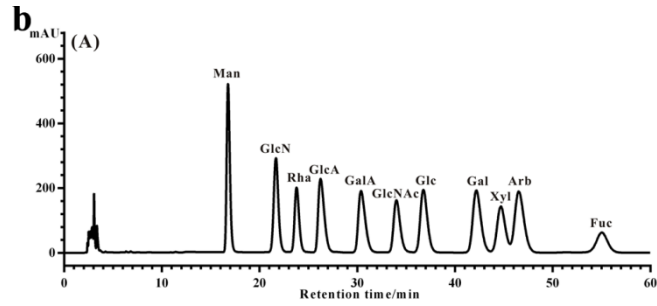
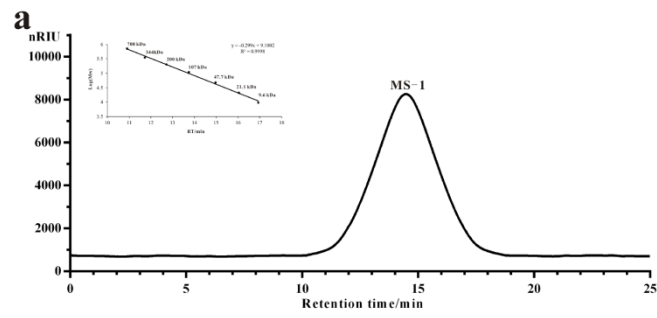


SUPPLEMENTARY TABLES

Table S1. ¹H and ¹³C chemical shifts data of DSMS-1.

Rhamnosyl residues	Nucleus	Chemical shift (ppm)					
		1	2	3	4	5	6
A→3)-α-L-Rhap-(1→	¹ H	5.00	4.20	3.89	3.60	3.91	1.38
	¹³ C	103.55	71.41	79.02	72.28	70.73	18.32
B→3)-α-L-Rhap-(1→	¹ H	5.07	4.18	3.89	3.60	3.91	1.38
	¹³ C	103.72	71.41	79.02	72.28	70.73	18.32
C→2)-α-L-Rhap-(1→	¹ H	5.23	4.11	3.93	3.56	3.98	1.35
	¹³ C	102.41	79.40	70.78	73.16	71.43	18.32
D→2)-α-L-Rhap-(1→	¹ H	5.30	4.11	3.93	3.56	3.98	1.35
	¹³ C	102.41	79.40	70.78	73.16	70.73	18.32
E→2,3)-α-L-Rhap-(1→	¹ H	5.39	4.27	3.97	3.55	3.94	1.35
	¹³ C	102.37	80.90	79.00	73.29	71.43	18.32

SUPPLEMENTARY FIGURE LEGENDS



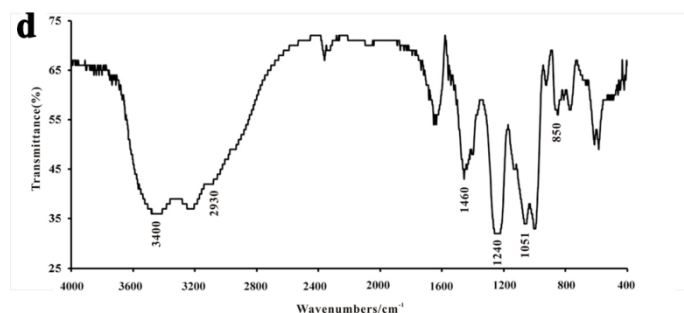
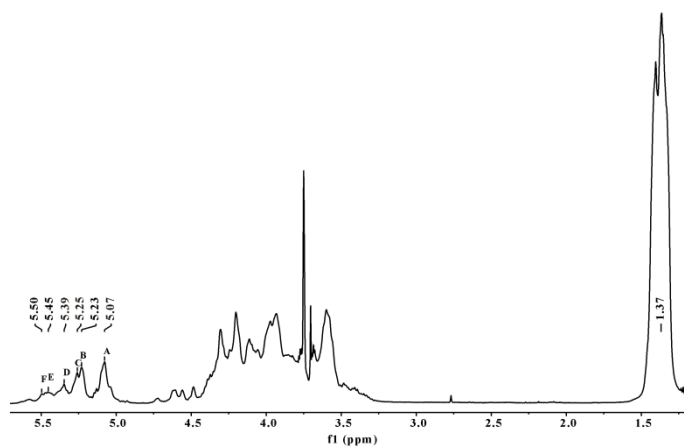
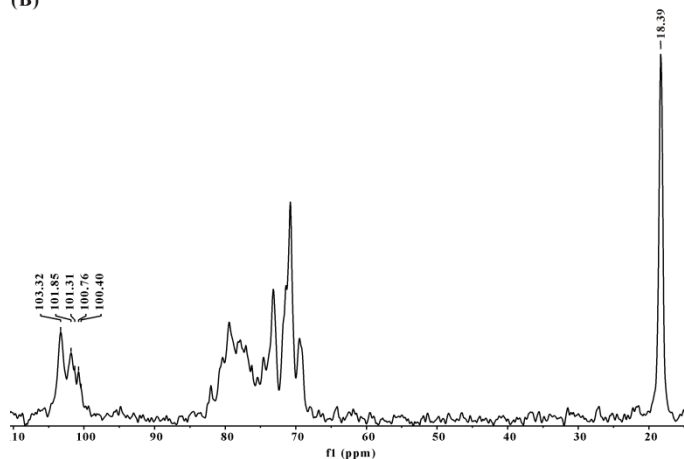


Figure S1. HPGPC chromatogram, HPLC chromatogram and IR spectrum of MS-1. (a) HPGPC chromatogram of MS-1 on a Shodex OHpak SB-804 HQ column and the standard curve of molecular weight; (b) HPLC chromatogram for monosaccharide composition analysis of MS-1 (Man: D-mannose, GlcN: D-glucosamine, Rha: L-rhamnose, GlcA: D-glucuronic acid, GalA: D-galacturonic acid, Glc: D-glucose, Gal: D-galactose, Xyl: D-xylose, Ara: L-arabinose, Fuc: L-fucose); (c) HPLC chromatogram of the sugar configuration determination of MS-1 (D-Rha: D-rhamnose, D-GlcA: D-glucuronic acid, D-Glc: D-glucose, D-Xyl: D-xylose, L-Rha: L-rhamnose); (d) IR spectrum of MS-1.

(A)



(B)



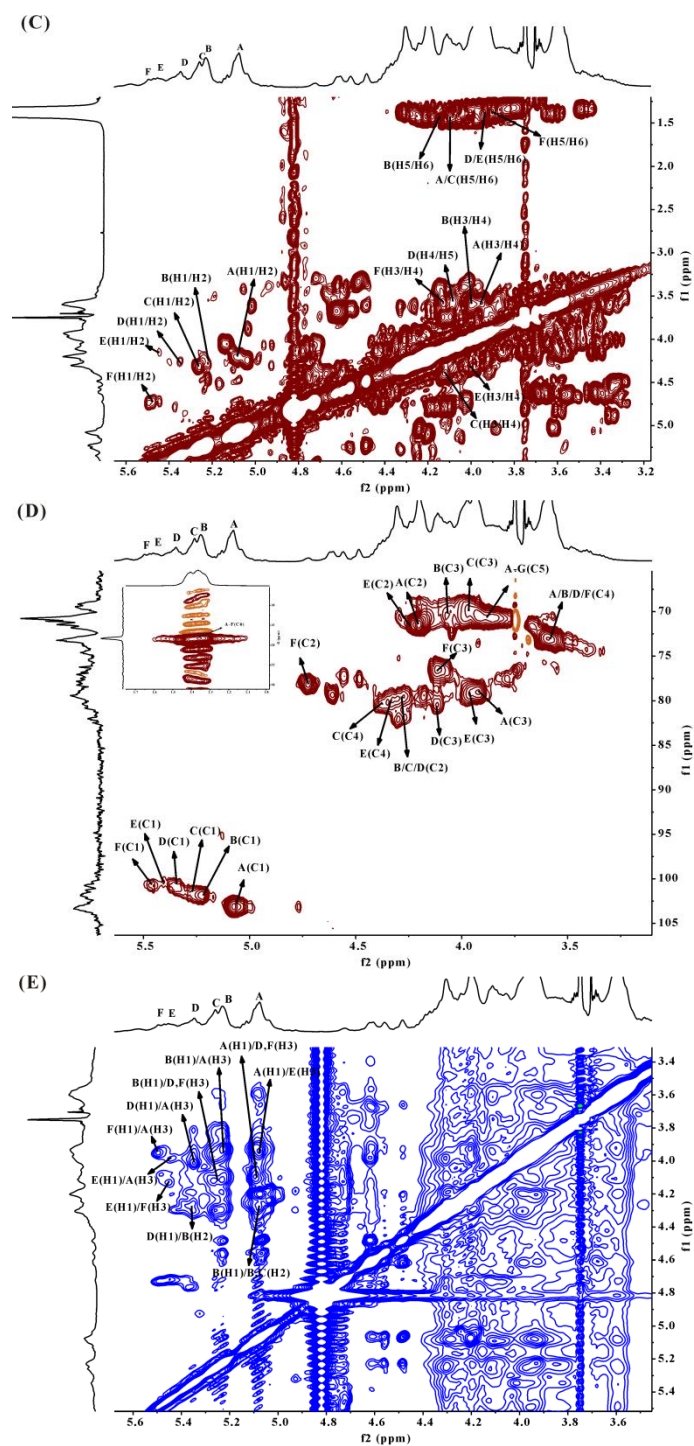


Figure S2. NMR spectra of MS-1. Spectra were performed on an Agilent DD2 500M NMR spectrometer. Chemical shifts are referenced to internal acetone at 2.225 ppm for ^1H and 31.07 ppm for ^{13}C . (A) ^1H NMR spectrum; (B) ^{13}C NMR spectrum; (C) ^1H - ^1H COSY spectrum; (D) ^1H - ^{13}C HSQC spectrum; (E) ^1H - ^1H NOESY spectrum. A-F correspond to $\rightarrow 3$ - α -L-Rhap-(1 \rightarrow , $\rightarrow 2$)- α -L-Rhap-(1 \rightarrow , $\rightarrow 2$)- α -L-Rhap(4SO $_4$)-(1 \rightarrow , $\rightarrow 2,3$)- α -L-Rhap-(1 \rightarrow , $\rightarrow 3$)- α -L-Rhap(4SO $_4$)-(1 \rightarrow and $\rightarrow 3$ - α -L-Rhap(2SO $_4$)-(1 \rightarrow , respectively. Rhap: rhamnopyranose.

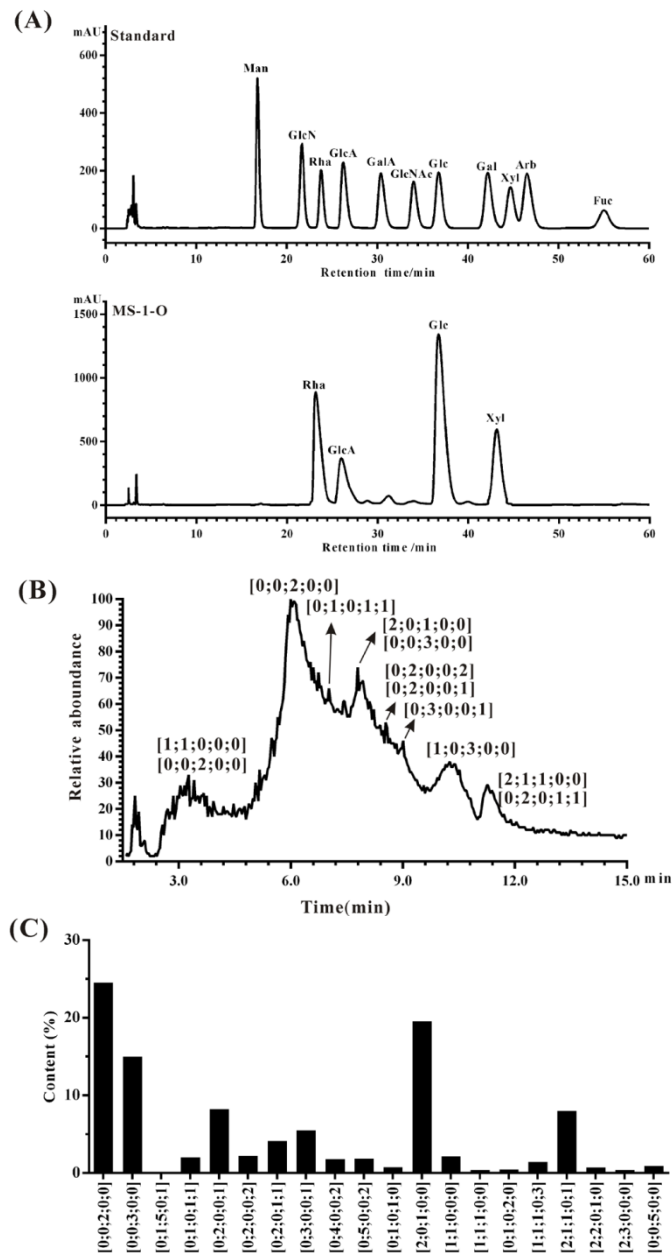
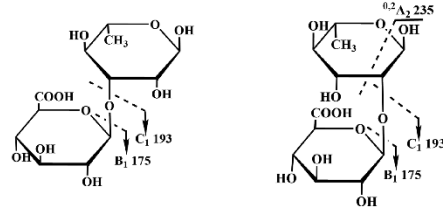
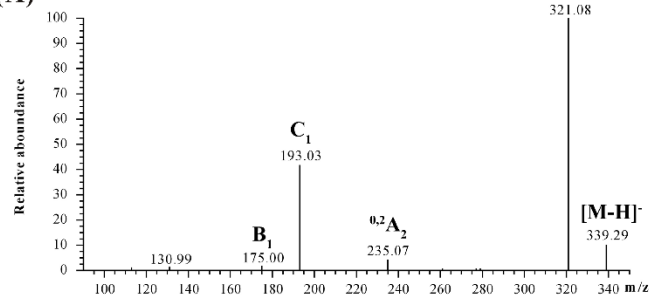
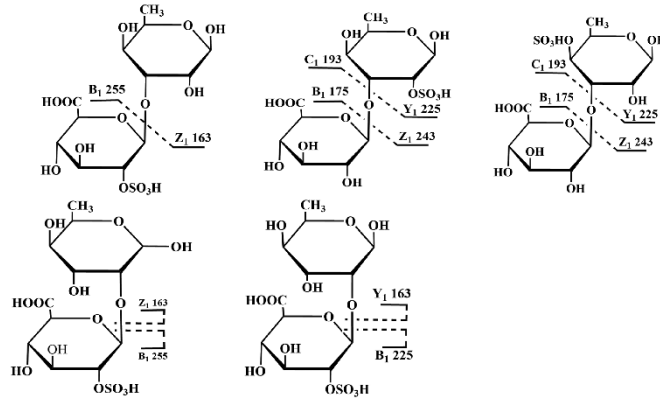
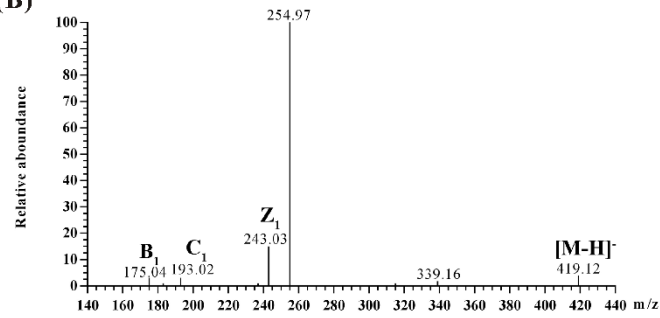


Figure S3. HILIC-FTMS profiling and HPLC chromatogram of MS-1-O. (A) HPLC chromatogram for monosaccharide composition analysis of MS-1-O (Man: D-mannose, GlcN: D-glucosamine, Rha: L-rhamnose, GlcA: D-glucuronic acid, GalA: D-galacturonic acid, Glc: D-glucose, Gal: D-galactose, Xyl: D-xylose, Ara: L-arabinose, Fuc: L-fucose); (B) total ion chromatography of MS-1-O; (C) composition analysis of MS-1-O calculated by GlycResoft. The analytical error for each oligosaccharide was < 5%. Oligomer composition was given as [Xyl; Rha; Glc; GlcA; SO₃].

(A)



(B)



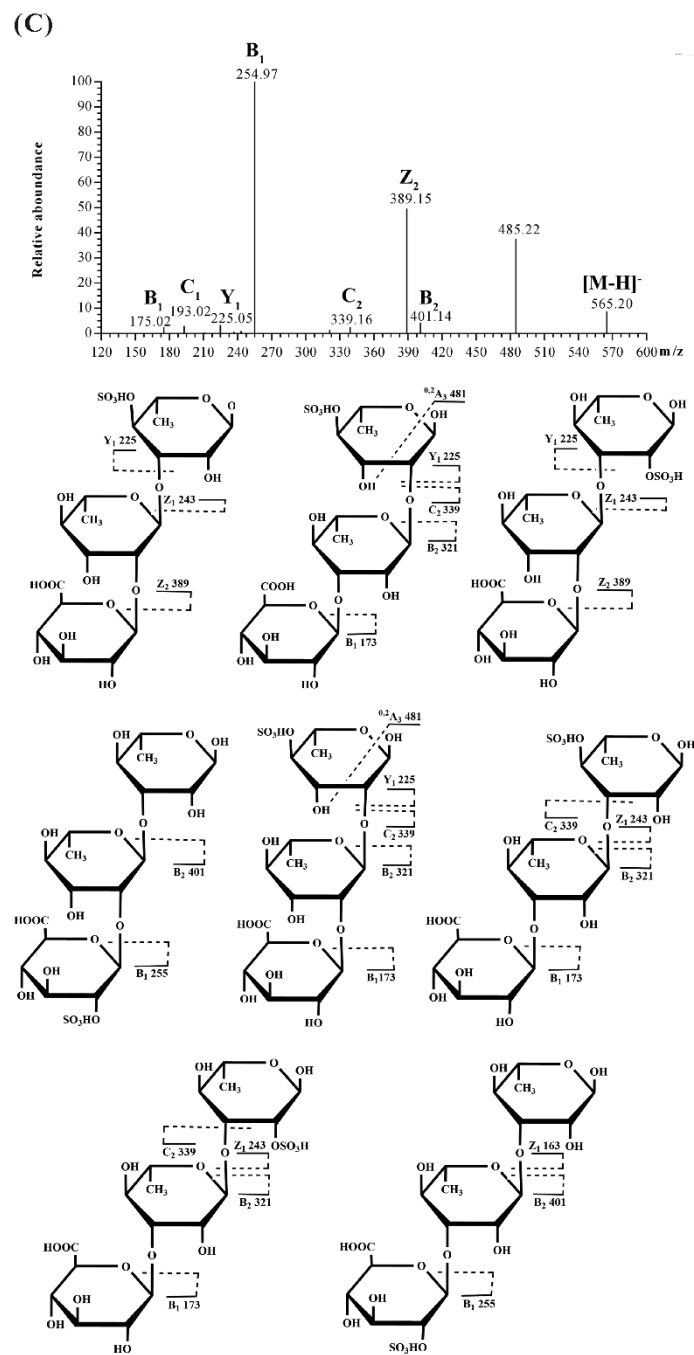


Figure S4. Negative-ion ES-CID-MS/MS/MS product-ion spectra and assignments of the ions. (A) ES-MS spectrum of ion at m/z 339; (B) ES-MS spectrum of ion at m/z 419; (C) ES-MS spectrum of ion at m/z 565.