Gas-Phase Fragmentation of Oligosaccharides in MALDI Laser-Enhanced In-Source Decay Induced by Thermal Hydrogen Radicals

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Supplementary Information

a. Hydrogen/Deuterium Exchange MALDI ISD Spectrum of Mannohexaose

Following deuterium exchange, the $[M + Na]^+$ peak of deuterium mannohexaose was shifted to give a cluster of isotopomer peaks centered around *m/z* 1027.40 (Fig. S1). This ion corresponds to $[M(^2H_{14}) + Na]^+$ and is evidence for the exchange of 14 protons. The occurrence of three deuterium exchanges on the monosaccharide residue at the non-reducing end was revealed by the mass difference of 164 Da between $[M + Na]^+$ (*m/z* 1027.40) and Y_5 (*m/z* 863.32). In Fig. S1, the mass differences of the adjacent Y-type ions (i.e., *m/z* 863.32, 699.27, 535.21, 371.14) were 164 Da, which is indicative of the two deuterium exchanges to occur on each of the second, third, and fourth monosaccharide residues from the nonreducing end of the oligosaccharide chain. The number of exchangeable hydrogen atoms of the two monosaccharide residues at the reducing end was 5, which was deduced by the mass difference between the native and deuterium-exchanged masses

(371-365-1=5) of Y_2 ion. The mass difference between $[M + Na]^+$ ion and $^{0,2}A_6$ ion (*m/z* 965.37) is 62 in Fig. S1, which is indicative of two deuterium exchange occurring on the free 1- and 2-OH groups. The *m/z* values of $^{2,4}A_6$ and $^{2,4}A_5$ ions were 61 mass units lower than those of $^{0,2}A_6$ and $^{0,2}A_5$ ions, respectively, which suggested that one deuterium exchange occurred on each of the free 6-OH groups of the two monosaccharide residues at the reducing end. Unfortunately, due to the absence of Y_1 ion, it was uncertain that one deuterium exchange occurred on the 2-OH group of the second monosaccharide residue or the 4-OH group of the first monosaccharide residue from the reducing end. Altogether 14 exchangeable hydrogen atoms were found for the fragments. Therefore, these results confirmed no deuterium deficit during ISD fragmentation, revealing that intramolecular proton/deuteron migration almost did not occur. This finding is in agreement with the observation made in a previous report about MALDI ISD fragmentation of peptides.[1]

In this spectrum (Fig. S1), B-type ions were at 20 mass units lower than adjacent Y-type ion, while the mass differences between them were 18 Da for the ISD spectrum of nonlabeled mannohexaose.[2] In contrast to adjacent B-type ions formed by elimination of hydrogen atoms of 2-OH groups, the Y-type ions, although containing more than one theoretical exchangeable hydrogen atom, showed an incorporation of two (20 – 18) deuterium atoms. Taking these results into consideration, one can conclude that the additionally transferred deuterium atom was abstracted intermolecularly from the deuterated matrix.

References

1 N. Bache, K. D. Rand, P. Roepstorff and T. J. D. Jørgensen, *Anal. Chem.*, 2008, 80, 6431.

2 H. Yang, Y. Yu, F. Song and S. Liu, *J. Am. Soc. Mass Spectrom.*, 2011, **22**, 845.

a. Hydrogen/deuterium exchange MALDI ISD spectrum of mannohexaose

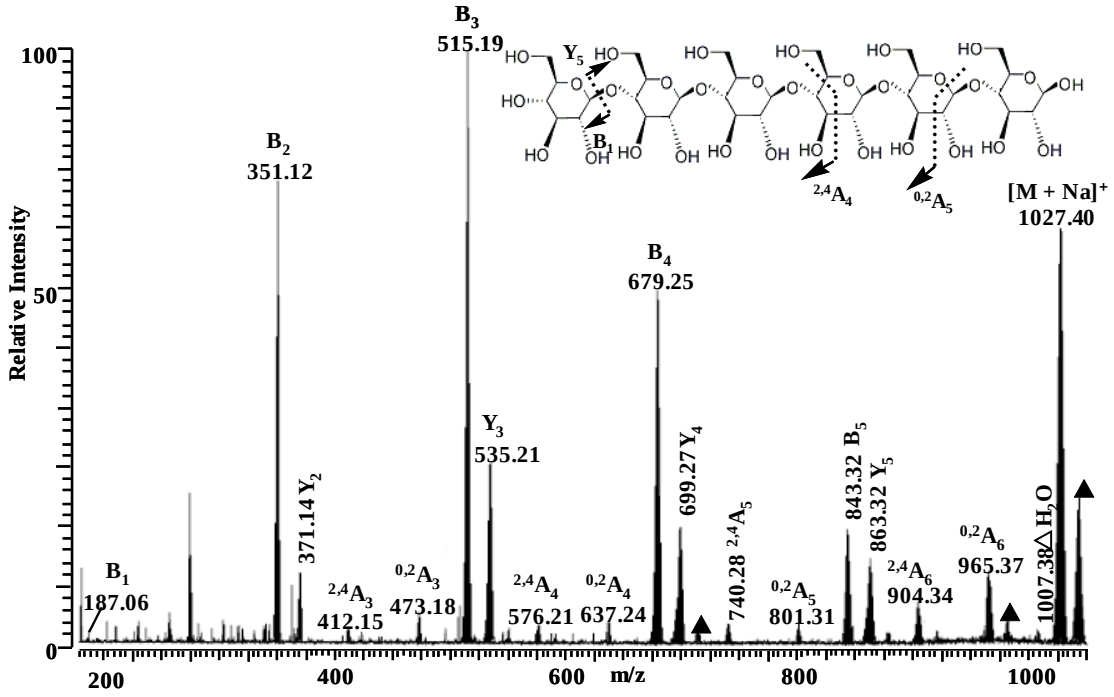


Fig. S1 Hydrogen-deuterium exchange MALDI LEISD mass spectrum of mannohexaose. Peaks labeled with solid triangles are potassium adduct ions.

b. The fragmentation yields of linear oligosaccharides with different chain lengths

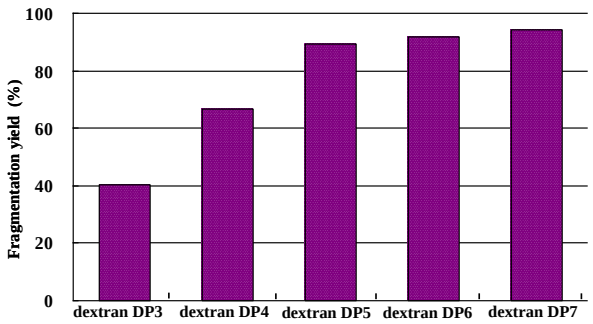


Fig.S2 The fragmentation yields in MALDI LEISD mass spectra of linear oligosaccharides with different chain lengths separated from dextran 1000 by HPLC using 3-AQ as matrix. DP indicates degree of polymerization.

c. MALDI LEISD mass spectrum of DM-β-CD

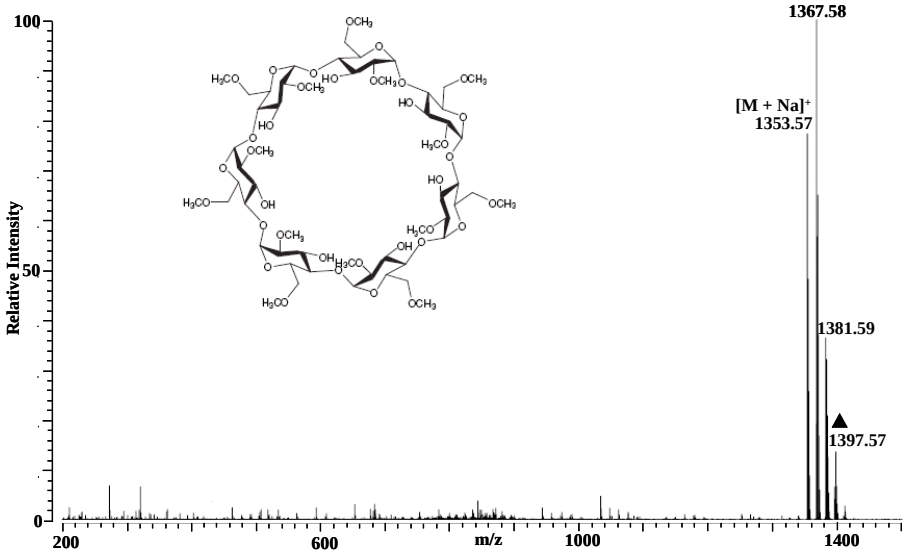
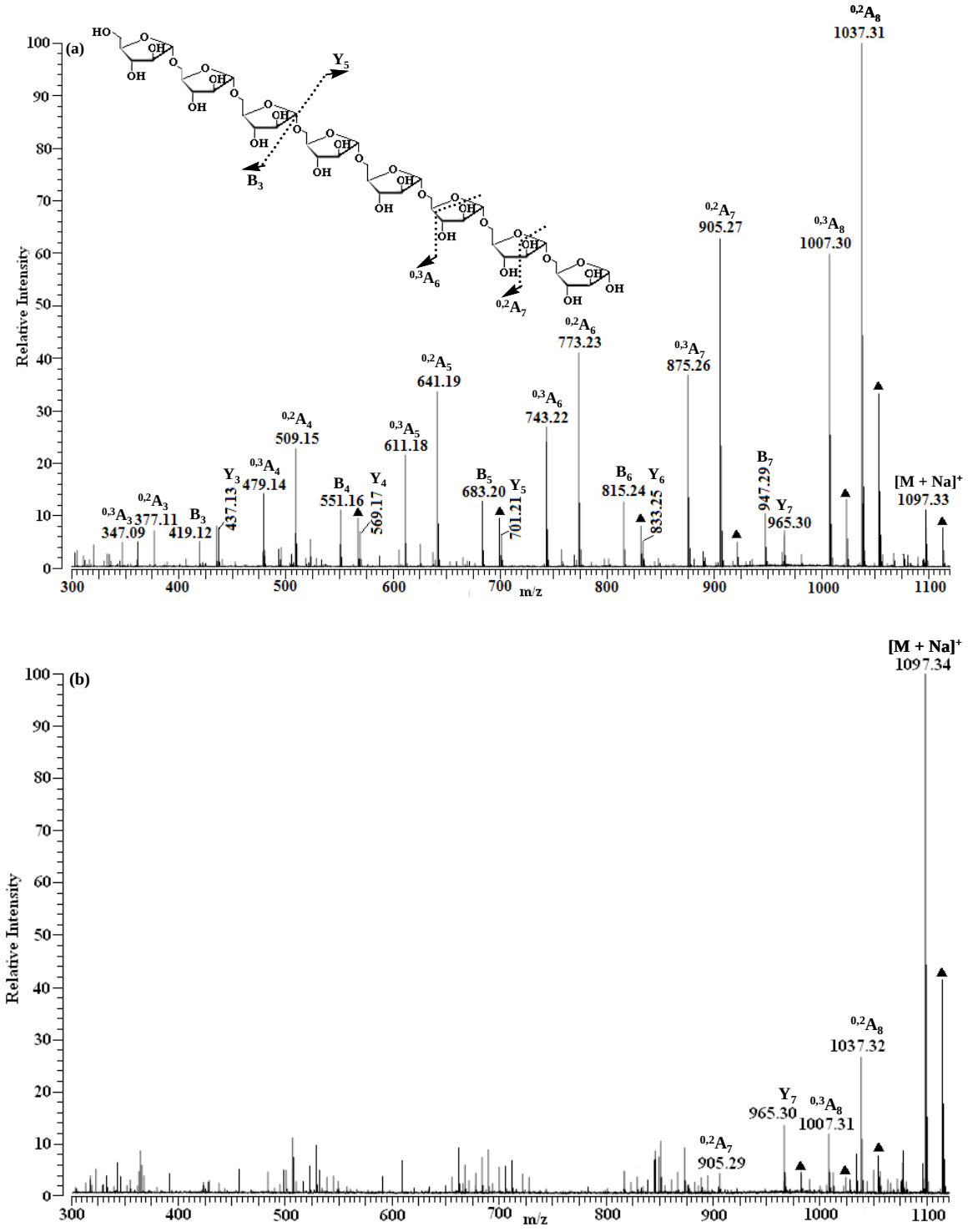
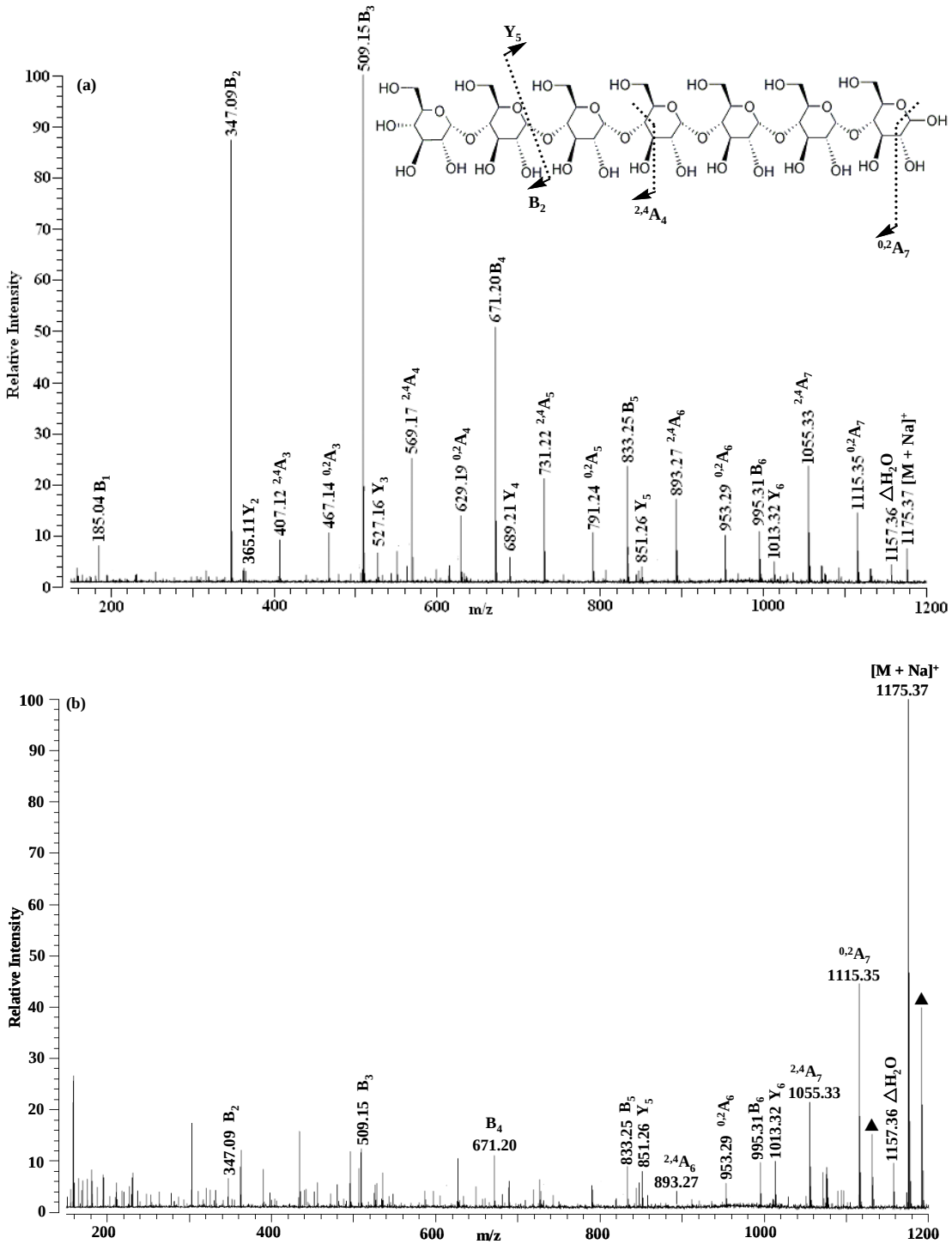


Fig. S3 MALDI LEISD mass spectrum of DM-β-CD. The peak labeled with solid triangle is potassium adduct ion.

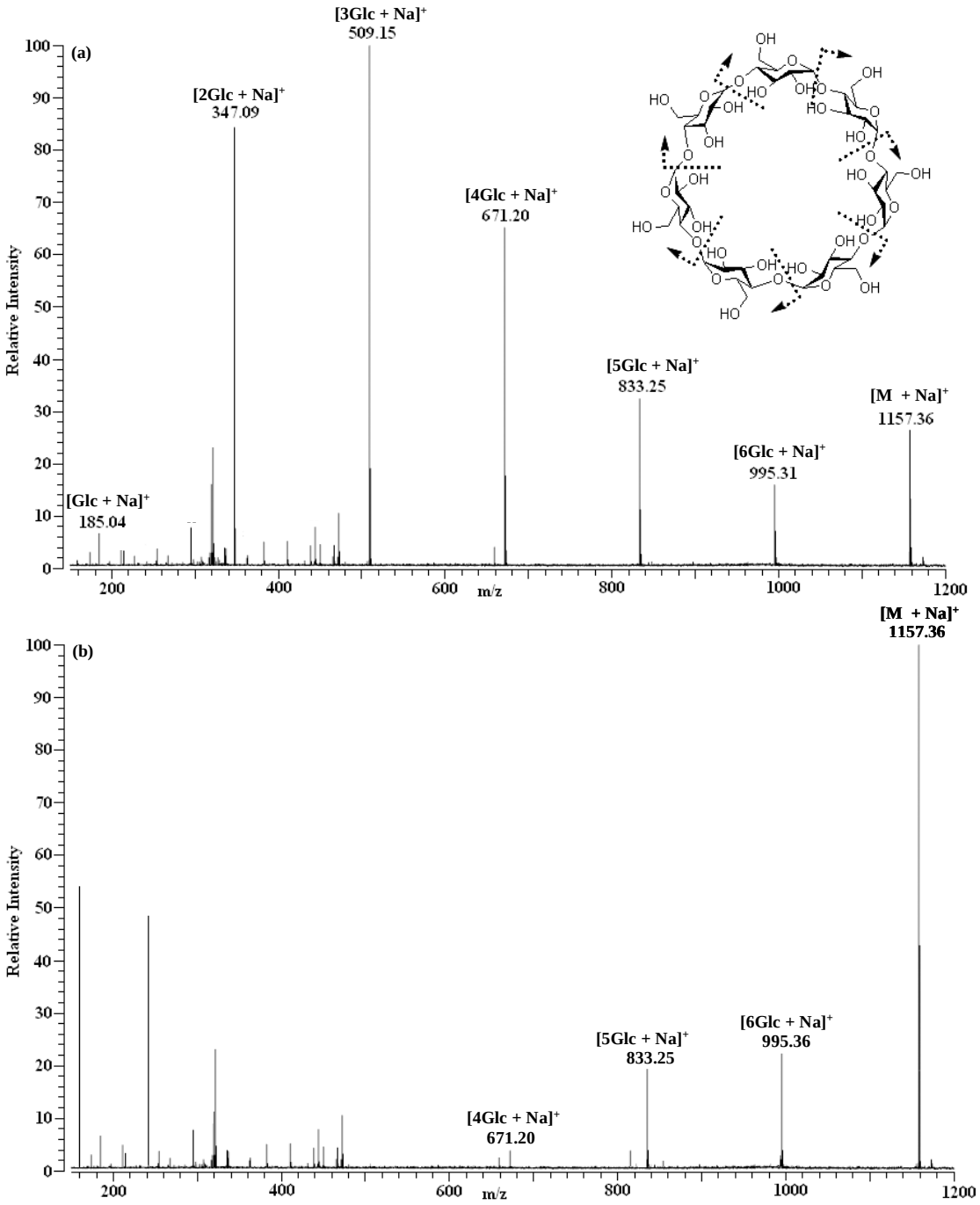
The LEISD mass spectra of the other used oligosaccharides are as follows:



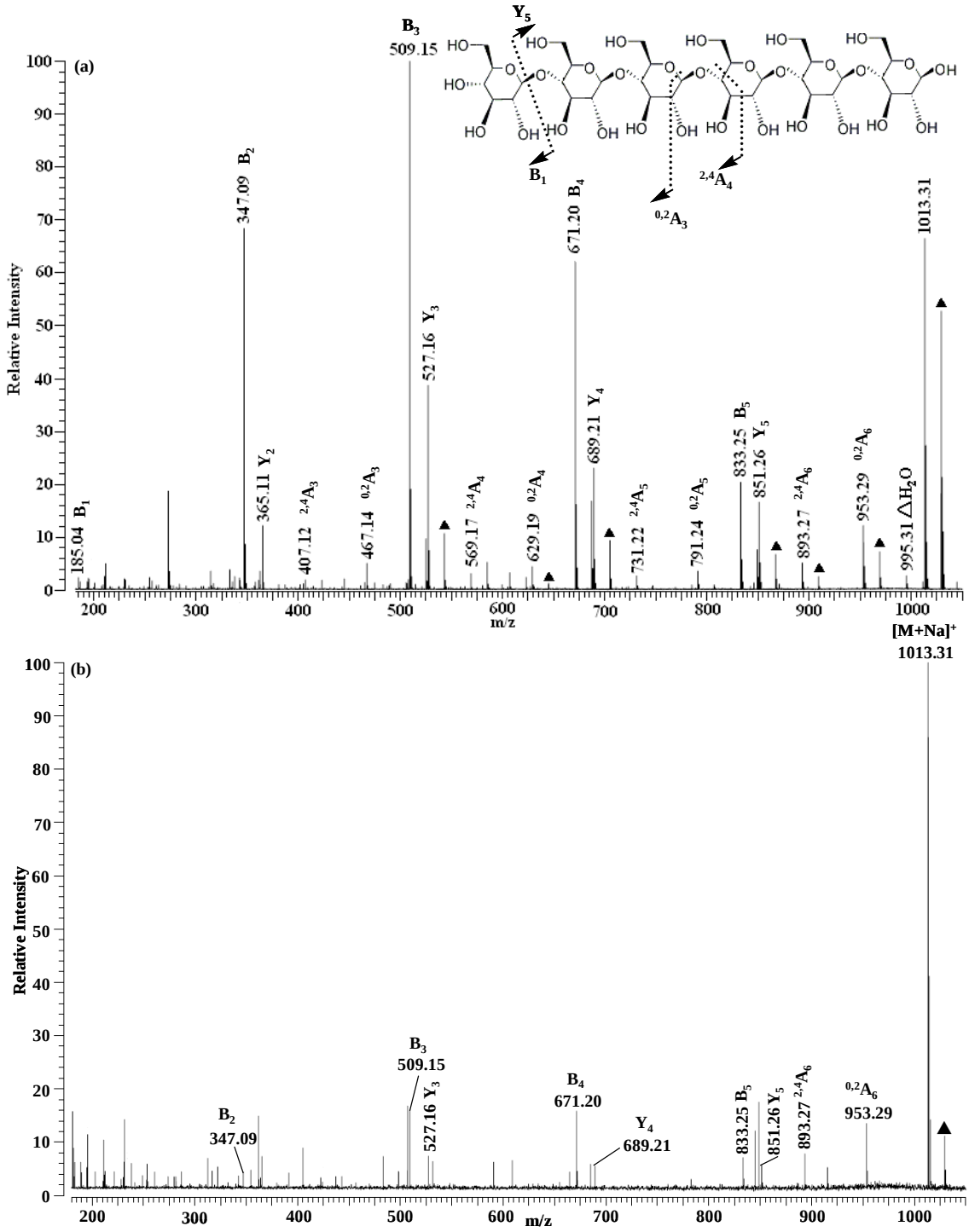
MALDI LEISD mass spectrum of arabino-octaose using (a) 3-AQ and (b) HPA as matrices. The peak labeled with solid triangle is potassium adduct ion.



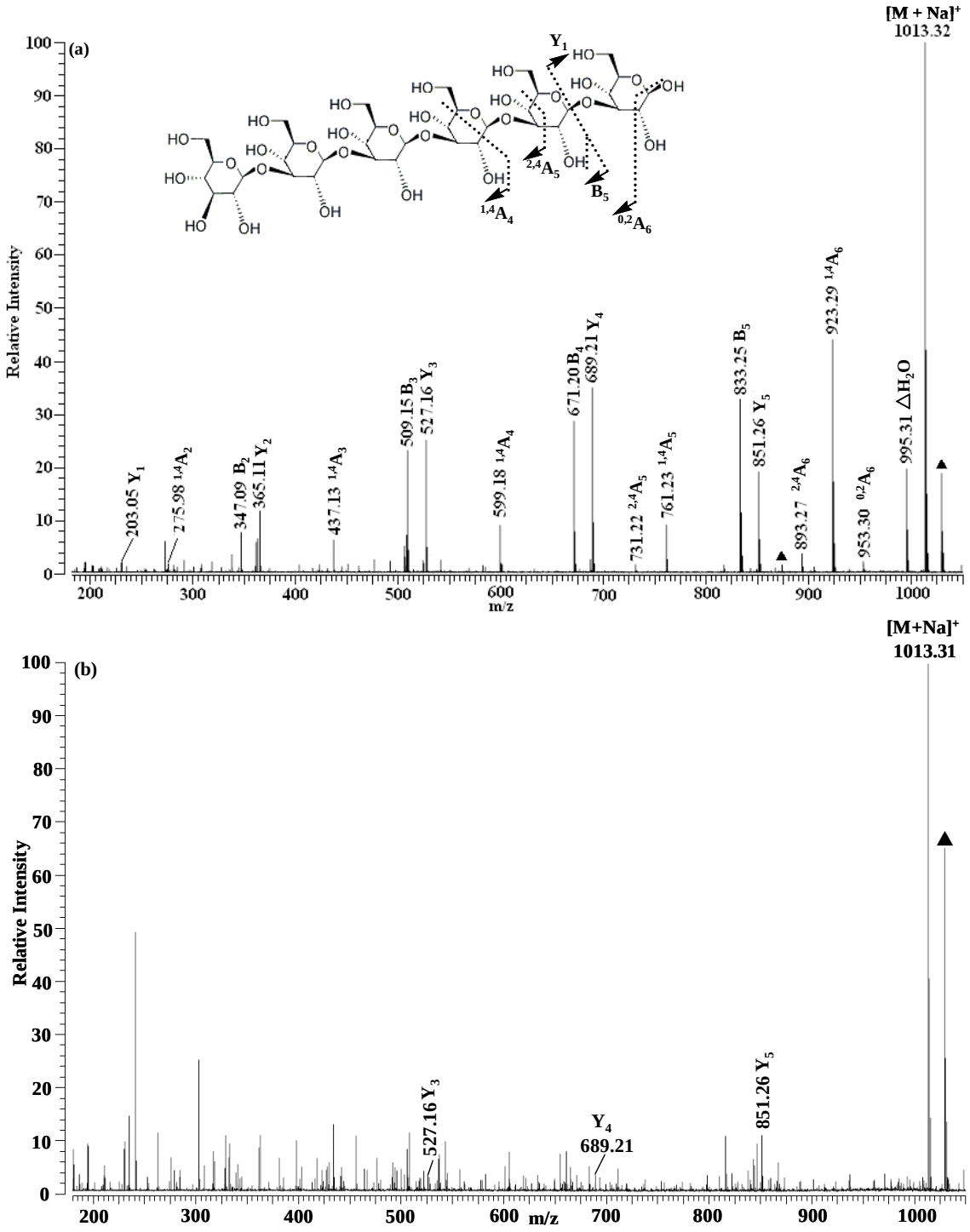
MALDI LEISD mass spectrum of maltoheptaose using (a) 3-AQ and (b) HPA as matrices. The peak labeled with solid triangle is potassium adduct ion.



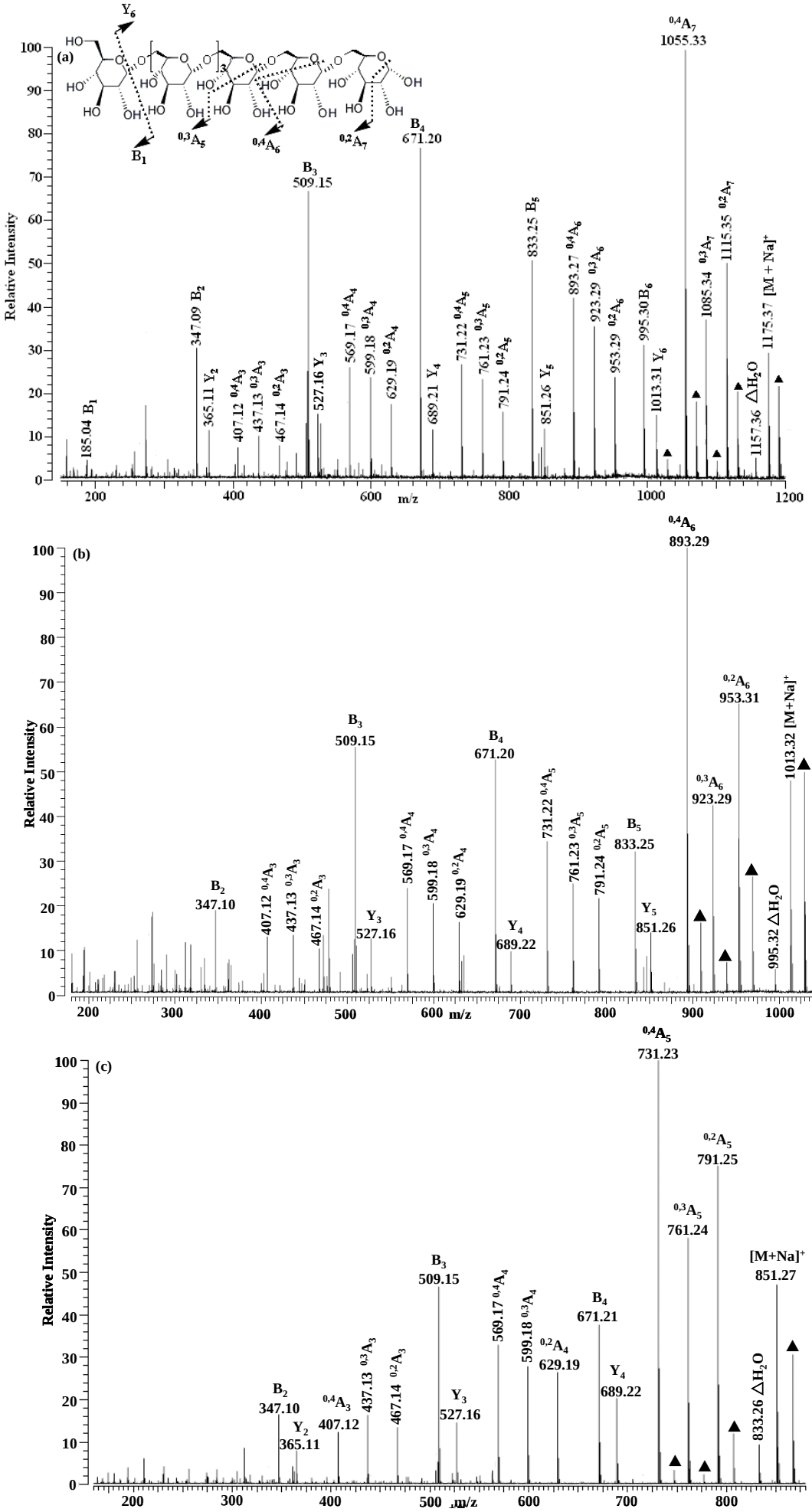
MALDI LEISD mass spectrum of β-CD using (a) 3-AQ and (b) HPA as matrices. The peak labeled with solid triangle is potassium adduct ion.

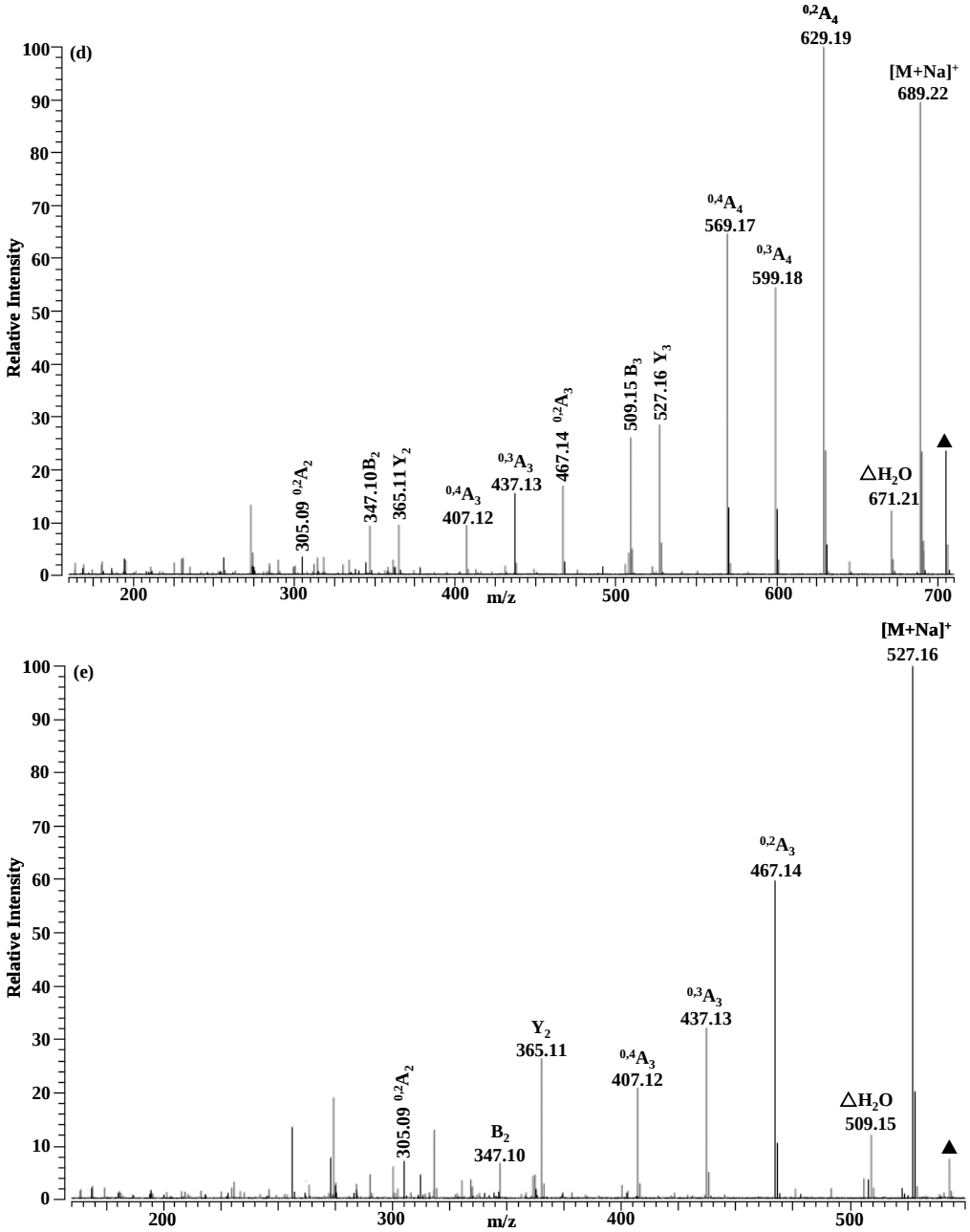


MALDI LEISD mass spectrum of mannohexaose using (a) 3-AQ and (b) HPA as matrices. The peak labeled with solid triangle is potassium adduct ion.



MALDI LEISD mass spectrum of laminarihexaose using (a) 3-AQ and (b) HPA as matrices. The peak labeled with solid triangle is potassium adduct ion.





MALDI LEISD mass spectrum of (a) dextran DP7, (b) dextran DP6, (c) dextran DP5, (d) dextran DP4, and (e) dextran DP3 using 3-AQ as matrix. The peak labeled with solid triangle is potassium adduct ion.