

A theoretical study on influence of linkage position on fragmentation reaction of mono fucosylated oligosaccharides

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【Introduction】 Oligosaccharides have many isomers and commonly found on the plasma membrane of animal cells where they can play a role in cell-cell recognition. Matrix-assisted laser desorption/ionization (MALDI)-multiple-stage mass spectrometry (MSⁿ) technique has been used for structural determination of oligosaccharide. Its negative-ion mode produces complementary information and can yield less ambiguous spectra¹⁾ than those provided by positive ion spectra. We have recently investigated the fragmentation processes of three kinds of isomeric oligosaccharides by using ultra accelerated tight-binding calculation. A possible fragmentation mechanism of Y-type cleavage has been proposed.

【Method】 “New-Colors”, an accelerated tight-binding calculation method, which is 10 million times faster than conventional first principles method, was used in our calculation. Total energy of a system contains the molecular orbital (MO) energy, columbic energy, and exchange-repulsion energy.

【Results】 We use the pyrene butanoic acid hydrazide labeled MFLNH as simulation molecule. Three isomeric compounds MFLNH-I (I), MFLNH-II (II) and MFLNH-III (III) were shown in Fig.1. Theoretical

calculations for those oligosaccharides were performed to investigate the reaction mechanism. By our method, deprotonation reactions on amide protons and all the hydroxyl groups were simulated. In the light of N-acetoamide play important role in stability of molecular ion and the acidity order (OH < HNAc), a possible mechanism of Y-type fragmentation is shown in Scheme 1. In this case, Y-type fragmentation is assumed to take place by electron from the ring oxygen attack the aromatic carbon, and consequently the Y-type fragment ion (R₁-O[⊖]) is generated.

1) J. Amano *et al*, *Glycobiology*. Vol. **19**, 592-600 (2009)

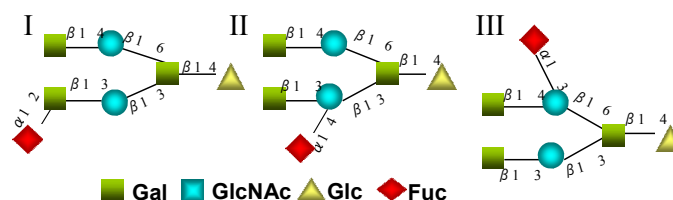
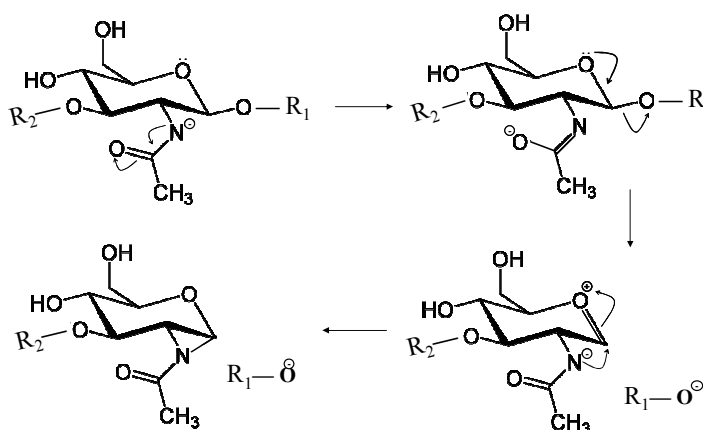


Fig. 1. Structures of the three isomeric oligosaccharides



Scheme 1. A proposed fragmentation mechanism of Y-type cleavage