# Scientific Report

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In this STSM we studied the fragmentation of deprotonated sugars using Matrix-Assisted Laser Desorption/Ionisation (MALDI). For this purpose we measured negative ion Time-of-Flight (TOF) mass spectra in Reflectron mode and additionally the metastable decay of deprotonated Ribose, different isotope-labeled Ribose molecules, Fructose and several Sugar-Phosphates. To gain more information on the decomposition sequence we also recorded the metastable decay of some fragment anions that are produced in-source.

The main fragments observed in MALDI-TOF of Ribose using Bisbenzimide as Matrix are $(M-H)^-$ (149 amu), $C_5H_5O_4^-$ (129 amu), $C_4H_4O_3^-$ (100 amu), $C_3H_3O_2^-$ (71 amu) and $C_2H_2O_2^-$ (58 amu). This fragmentation pattern is very similar to the Dissociative Electron Attachment (DEA) spectra of Ribose obtained previously in Berlin. The general tendency is a shift of one mass unit indicating that the abstraction of neutral fragments is comparable in the parent ion $M^-$ and in the deprotonated parent $(M-H)^-$.

In Post-Source-Decay (PSD) the deprotonated Ribose ion was selected and its decomposition recorded. The dominant signals are assigned to $C_5H_7O_4^-$ (131 amu) and $C_3H_5O_3^-$ (89 amu). Additional fragment anions with less intensitiy in the PSD spectra of $(M-H)^-$ are $C_5H_7O_4^-$ (131 amu), $C_4H_7O_4^-$ (119 amu), $C_5H_5O_3^-$ (113 amu), $C_4H_4O_3^-$ (100 amu), $C_2H_5O_3^-$ (77 amu) and $C_3H_3O_2^-$ (71 amu).

By means of Ribose labeled with $^{13}C$ and D, respectively, at the first carbon (C1) and $^{13}C$ at C5 a shift of several signals was observed. This indicates that (a) the observed masses in the TOF-Reflectron spectra originate indeed from the sugar molecules and (b) the generation of some fragments like $C_4H_4O_3^-$ proceeds highly selective with the negative charge remaining on the C1 site of the molecule.

To expand our investigation to molecules that are closer to the DNA backbone we furthermore studied metastable decay of deprotonated 5-Ribose-phosphate, 5-Deoxyribose-phosphate and 1,6-Fructose-bisphosphate. The main fragmentation channel is the abstraction of the phosphate group(s) with the negative charge remaining either on the phosphate group or the sugar unit.

These results are very valuable for the understanding of fragmentation of negative ions of DNA constituents and are supposed to be published in two forthcoming articles.