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Application of the gas-phase reactivity of Pb\(^{2+}\) ions to the structural characterization of disaccharides

Jean-Yves Salpin, Marie Laffitte, Jeanine Tortajada

Introduction

Oligosaccharide analysis is a challenging task for mass spectrometry. A complete structural description of carbohydrates implies not only exact mass measurement, sites and anomeric configuration of the glycosidic linkages, and also stereochemical characterization of the different asymmetric centers of the sugar ring. Many studies have been carried out on those topics for more than three decades. With the advent of soft ionization techniques, it has been shown that structural isomers can be differentiated when coordinated to certain metal ions. Lead cationization has proven to be particularly useful in the structural differentiation of monosaccharides.\(^{[1]}\) The present study aims to examine if the lead reactivity can be also used to characterize the glycosidic linkage. To this end the results obtained with a series of disaccharides are presented.

Methodology

Mass Spectrometry

- Triple-quadrupole mass spectrometer (Applied Biosystems MDQ/SCIEX API 2000) fitted with a "Turbobiflex" source.
- Aqueous solutions of Pb(NO\(_3\))\(_2\)/disaccharide (5·10\(^{-3}\) mol L\(^{-1}\)/10\(^{-4}\) mol L\(^{-1}\)).
- Flow rate: 5μl/min.
- MS/MS experiments with N\(_2\) as collision gas (P = 2·10\(^{-3}\) Torr).

Molecular orbital calculations

- Preliminary step: PM3 semi-empirical calculations in order to locate the best coordination sites (residues in their \(\chi_1\) conformation).
- DFT calculations with the B3LYP hybrid functional. Geometry optimization and vibrational analysis at the B3LYP/6-31G(d) level.
- Stuttgart basic set and quasi-relativistic pseudo-potential to describe Pb atom.
- NBO analysis.

Results

- Three series of ions observed:
  - Pb\(^{2+}\)glyco: \(m/2 = 549, 891\) (series 1).
  - \([\text{Pb}/\text{disaccharide}] – \text{H}^+\) ions: \(m/2 = 387, 369\) (series 2).
  - \([\text{Pb}/\text{disaccharide}] – \text{H}^+\) ions: \(m/2 = 387, 369\) (series 3).

- MS/MS spectra repeated 10 times for each disaccharide to check the reproducibility of the intensities.

- Structural distinction of the disaccharides based on the MS/MS spectra of the \([\text{Pb}/\text{disaccharide}] – \text{H}^+\) ions (\(m/2 = 549\)).

- Residual intensity of the parent ion set to 25 % by varying the collision energy, all the other parameters being kept constant.
- MS/MS spectra repeated 10 times for each disaccharide to check the reproducibility of the intensities.

The results are summarized below (peak areas relative abundances below 4 % are not taken into account).

<table>
<thead>
<tr>
<th>Name</th>
<th>Type</th>
<th>Parent ion</th>
<th>Fragment ion</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-glucosamine</td>
<td>D-glucosamine</td>
<td>m/z 549</td>
<td>m/z 387, 369</td>
</tr>
<tr>
<td>D-galactosamine</td>
<td>D-galactosamine</td>
<td>m/z 549</td>
<td>m/z 387, 369</td>
</tr>
<tr>
<td>D-mannose</td>
<td>D-mannose</td>
<td>m/z 549</td>
<td>m/z 387, 369</td>
</tr>
<tr>
<td>D-glucose</td>
<td>D-glucose</td>
<td>m/z 549</td>
<td>m/z 387, 369</td>
</tr>
<tr>
<td>D-fructose</td>
<td>D-fructose</td>
<td>m/z 549</td>
<td>m/z 387, 369</td>
</tr>
<tr>
<td>D-maltose</td>
<td>D-maltose</td>
<td>m/z 549</td>
<td>m/z 387, 369</td>
</tr>
</tbody>
</table>

- NBO analysis: net charge of Pb 1.43
- Natural electronic configuration of Pb (lons)[(1S,13S)(1P,5S)]\(^{12}\)

DFT study

- Assuming this particular bonding scheme, deprotonation of either the first or the second monosaccharide unit leads to nearby degenerated structures. Consequently, fragmentations may inoffensively occur on each residue.
- NBO analysis: not charge of Pb 1.43
- Natural electronic configuration of Pb (lons)[(1S,13S)(1P,5S)]\(^{12}\)

Perspectives

- Isofocusing labeling experiments are in progress in order to examine in detail the mechanisms of fragmentation.
- Use of other metal ions.
- Analysis of bigger oligosaccharides.

Bibliography