The Effect of Stereoisomeric Structure on Retention Time in Gas Liquid Chromatography of Per-O-trimethylsilyl Derivatives of Pentoses and Hexoses

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The analysis of relationships between structure and retention time in gas liquid chromatography of pentoses and hexoses leads to the formulation of following rule: the per-O-trimethylsilyl derivatives of aldoses stereoisomers with conformational stability, identical ring form and the same number of substituted OH groups are longer retained on polar columns when the equatorial substituents are more numerous and are located nearer to the anomeric carbon.

Gas liquid chromatography provides an excellent mean for the analysis of sugars and its derivatives. Thus, not only the different pentoses or hexoses resulting from the variable disposition of OH groups at C-2,3 (respecively C-2,3,4), but also their α and β anomers and pyranose-furanose forms are partly or completely separated. These separation characteristics may disturb quantitative estimations in complex sugar mixtures of biological origin e.g. hydrolysats of mucosubstances from body fluids, especially because of the chromatographic interference of some of the anomers present in aqueous solutions (GHEORGHIU et al.1—3). The analysis of relationships between isomeric structure and the corresponding retention time is therefore of peculiar interest.

Based on the observation of KLEIN and BARTER 4, BISHOP 5 postulated that for polymethyl ethers of methyl glycopyranosides the anomer in which the C-1 methoxy group is placed in trans position to a C-2 substituent or in cis to an unsubstituted OH group at C-2 has the lower retention time. SWEELley et al. 6 showed that this generalization can not be extended to per-O-trimethylsilyl derivatives of pentoses and hexoses; in this case, when the sugar appears normally in one of the chair forms C1 or 1C and does not manifest important conformational instability, the anomer with the equatorial OH group at C-1 discloses the longest retention time.

In 2 previous papers 7, 8 we presented results in gas chromatographic analysis of sugar-containing compounds of biological fluids and their hydrolysis. Our observations suggest a more general formulation of the relationship between retention time and structure, applicable — for the pentoses and hexoses examined — not only to anomers, but also to their other stereoisomers. One has to consider in addition to the equatorial position of the glycosidic O-trimethylsilyl substituent all other trimethylsilyl groups located equatorially. It appears to be a rule, using polar columns *, that retention times of isomeric aldoses with a stable identical ring form (and with the same number of substituted OH groups) increase when the groups with equatorial position are more numerous and/or when they are located nearer to C-1 (Table 1).

Table 1 also shows that the effect caused by the number of equatorial substituents is generally by far greater than that of their position relatively to

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Table 1. The effect of isomeric structure on retention time in gas chromatographic analysis of per-O-trimethylsilyl derivatives of some monosaccharides.  

<table>
<thead>
<tr>
<th>Sugar</th>
<th>Conformation of the ring</th>
<th>Equatorial O-TMS groups</th>
<th>Relative retention times&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Number</td>
<td>Position</td>
</tr>
<tr>
<td>(Methyl)pentoses</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-L-arabinose</td>
<td>1 C (?)</td>
<td>1</td>
<td>+</td>
</tr>
<tr>
<td>α-L-fucose</td>
<td>1 C</td>
<td>2</td>
<td>+</td>
</tr>
<tr>
<td>β-L-arabinose</td>
<td>1 C (?)</td>
<td>2</td>
<td>+</td>
</tr>
<tr>
<td>α-D-xylose</td>
<td>C1</td>
<td>3</td>
<td>+</td>
</tr>
<tr>
<td>β-L-fucose</td>
<td>1 C</td>
<td>3</td>
<td>+</td>
</tr>
<tr>
<td>β-D-xylose</td>
<td>C1</td>
<td>4</td>
<td>+</td>
</tr>
<tr>
<td>Hexoses</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-D-mannose</td>
<td>C1</td>
<td>2</td>
<td>+</td>
</tr>
<tr>
<td>α-D-galactose</td>
<td>C1</td>
<td>2</td>
<td>+</td>
</tr>
<tr>
<td>β-D-mannose</td>
<td>C1</td>
<td>3</td>
<td>+</td>
</tr>
<tr>
<td>β-D-galactose</td>
<td>C1</td>
<td>3</td>
<td>+</td>
</tr>
<tr>
<td>β-D-glucose</td>
<td>C1</td>
<td>4</td>
<td>+</td>
</tr>
</tbody>
</table>

C-1; the retention time differences between classes with 1, 2, 3 or 4 such groups are increasing non-linearly. The respective figures point to the influence of other known conformational factors too: a supplementary equatorial substituent may have a very different action depending on the general molecular constellation (e.g. between α-galactose and α-glucose this difference is minimal as compared to that between β-galactose and β-glucose). The oxidation of an OH group, its replacement or any change in cyclic structure of sugars may of course greatly disturb these relationships. Galactose derivatives for example are eluted from polyethylene glycol succinate columns in the following order: 6-deoxy (γ, α, β) → γ peak (aldofuranose?) → aldopyranose (α, β) → 2-deoxy-2-amino (γ, α, β) → hexuronic acid (as methyl ester) → hexuronic acid lactone → 2-deoxy-2-acetamido (γ, α, β).