CONFORMATION STUDIES OF ^{13}C ISOTOPE LABELED DISACCHARIDES

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Introduction

The knowledge of the secundary structure of oligo- and polysaccharides is important in understanding how enzymes and other proteins interact with carbohydrates on the cell surface. By conformation analysis it is possible to obtain a picture of the three dimensional structure of a saccharide, which is described by the ring flexibility, the glycosidic (ϕ and ψ) and hydroxy methyl torsions (ω) (Figure 1).

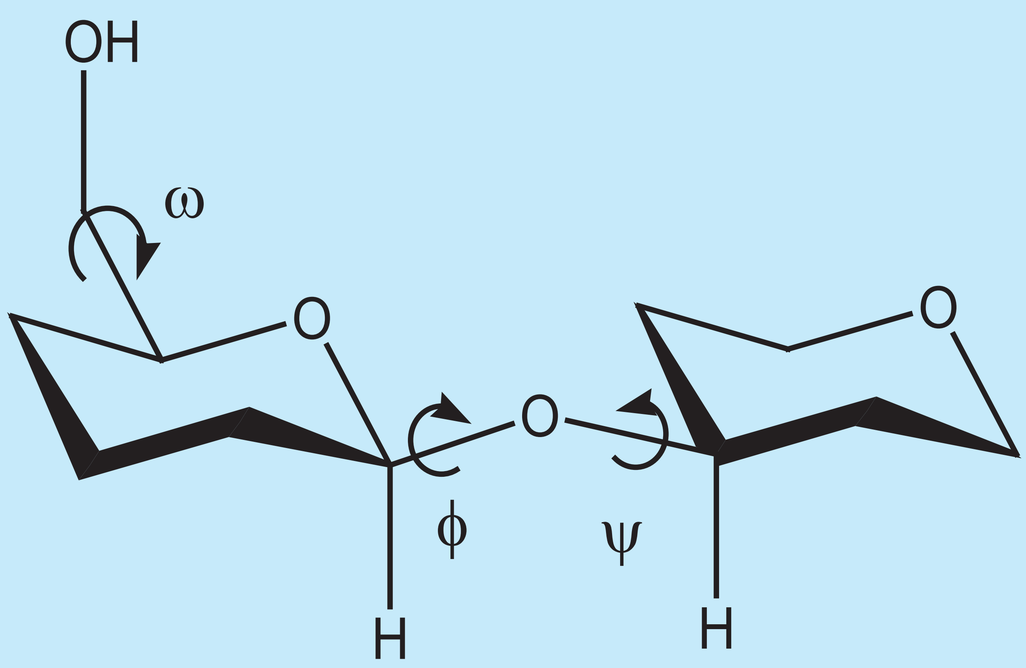

Figure 1. The torsion angles that describes the overall conformation in a saccharide.

In general, the value of ϕ depends on the exo-anomeric effect and ψ on steric effects and the ability to form hydrogen bonds, internal or external. Therefore, as a rough guideline, ϕ values are around -60° for α-D and β-D hexoses and about +60° for α-L and β-D hexoses, whereas ψ are usually between -50° and +50°.

The three staggered rotamers of ω are refered to as *gt* ($\omega \approx$ +65°), *gg* ($\omega \approx$ -65°) and *tg* ($\omega \approx$ 180°) (Figure 2).

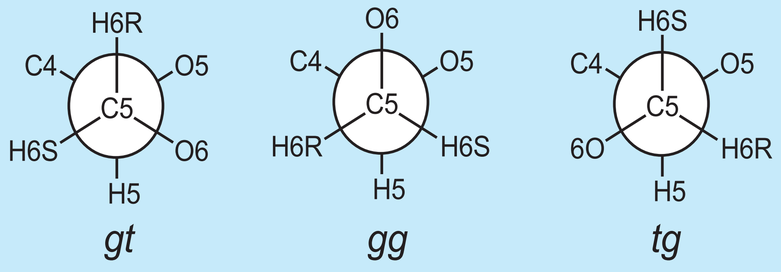

Figure 2. C5-C6 rotamers.

Nuclear magnetic resonance (NMR) is a powerful and easy method to performe conformation analysis. For example, the size of $^{3}J_{CH}$ is dependent on the torsion angles around a defined bond and the relation is described by the Karplus equation.[1] However, the value of the $^{3}J_{CH}$ can correspond to more than one torsion angle, because of the periodicity of the equation. Values of $^{3}J_{CC}$ in combination with $^{3}J_{CH}$ gives fewer possible torsions and therefore a better estimation of the preferred conformations. To measure $^{3}J_{CC}$ values it is necessary to syntezise ^{13}C labeled saccharides, due to the low natural occurrence of ^{13}C.

Experimental

The syntesis of the ^{13}C labeled and the unlabeled β-D-Glc*p*-(1$\rightarrow$3)-α-D-Glc*p*-OMe was performed from [1-^{13}C], [2-^{13}C] labeled and ordinary D-Glucose respective as the donor starting material, via regioselective coupling to position 3 of the acceptor.[2] In the last step the protecting groups are removed to obtain the unprotected saccharide which then are used for conformation analysis (Figure 3).

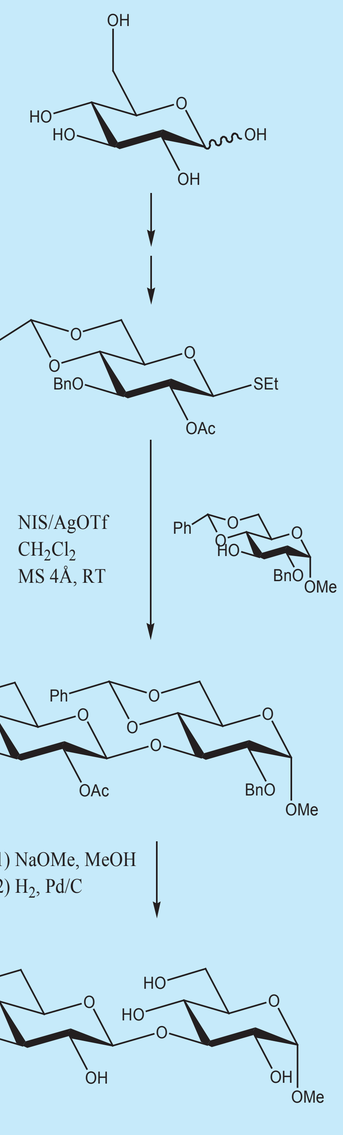

Figure 3. The syntetic route for β-D-Glc*p*-(1$\rightarrow$3)-α-D-Glc*p*-OMe.

Shortly, labeled and unlabeled β-D-Glc*p*-(1$\rightarrow$2)-α-D-Glc*p*-OMe, β-D-Glc*p*-(1$\rightarrow$4)-α-D-Glc*p*-OMe and β-D-Glc*p*-(1$\rightarrow$6)-α-D-Glc*p*-OMe will also be syntezised and subject to conformation analysis.

References

[1] M. Karplus, *J. Chem. Phys*. **1958**, *30*, 11-15

[2] G. H. Veeneman, S. H. van Leeuwen, J. H. van Boom, *Tetrahedron Letters* **1990**, *31*, 1331-1334.