

Analysis of Interaction between Glucose Anomers and Water Molecules

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Summary:

Glucose is the most widely used monosaccharide in living organisms. The stereochemical isomers that have different position of OH group on the C1 carbon (axial: α , equatorial: β), are termed anomers. Equilibrated glucose solution contains β -D-Glucose (~62%) and α -D-Glucose (~38%), and the stability is thought to depend on the hydrogen bond with surrounding water molecules. The aim of this study is to elucidate the effect of the interaction between carbohydrate and water on these structures using near-infrared spectroscopy. To analyze the spectra of these two anomers, we measured the solution using NIR spectrophotometer and polarimeter simultaneously. Moreover, we used deuterated glucose in order to clarify the origin of the spectral peak. These results showed that these anomers have obvious difference on C-H region and the absorbance at 1,742 nm has a strong correlation with the ratio of anomer. It suggests that this absorbance reflects the structure of anomers and is useful for quantification of glucose anomers.

Introduction:

Carbohydrate is one of the most important materials in living organisms, and especially glucose is widely used in energy storing, cell structure and molecular recognition. Hexose like glucose has stereochemical isomer, termed anomers, in aqueous solution and equilibrated glucose solution contains β -D-Glucose (~62%) and α -D-Glucose (~38%) (Figure 1). The stability of each anomer in solution is determined depending on hydrogen bonding with water molecules and is different from that in gas or crystal. In this study, we analyzed the near-infrared spectra of both glucose anomers in order to elucidate the difference of the water structure around each glucose anomer.

Materials and Methods:

Sample α -D-Glucose (96%, Sigma-Aldrich, St.Louis, MO, USA) and β -D-Glucose (98%, Cayman Chemical, Ann Arbor, MI, USA) were used to compare anomers. D-glucose-1-d₁ (98%, Sigma-Aldrich, St.Louis, MO, USA) and D-glucose-6,6-d₂ (98%, Sigma-Aldrich, St.Louis, MO, USA) were used to clarify the origin of spectral peak. 200 mM sugar solution was prepared just before measurement.

Spectral acquisition A NIR spectrophotometer MPA (Bruker Optics, Ettlingen, Germany) was used for spectral acquisition. The NIR spectra were measured with cuvettes in the wavelength region of 12,000 cm⁻¹ (833 nm) to 4,000 cm⁻¹ (2500 nm) with 8 cm⁻¹ intervals. A polarimeter RePo-5 (Atago, Tokyo, Japan) was used to acquire the optical rotation.

Data analysis Data analysis was performed with Pirouette software (Infometrix, Bothell, WA, USA). Spectral pretreatments of smoothing and first derivative were applied. Principal component analysis (PCA) and partial least squares (PLS) regression was performed.

Results and Discussion:

NIR spectra of α -D-Glucose and β -D-Glucose solution showed obvious difference and the difference in C-H region has a concentration dependency. On the PLS regression analysis with optical rotation, a linear regression model with a high accuracy was developed using near-infrared spectral data, and absorbance at 1,742 nm showed highest peak in regression vector (Figure 2). Moreover, absorbance at 1,742 nm had a strong correlation with the optical rotation after normalization for spectra (Figure 3), suggesting this absorbance reflects the structure of anomers and is useful for quantification of glucose anomers. In addition, the correlation between absorbance at 1,742 nm and optical rotation was kept both in the measurement at 37°C and using PBS buffer as a solvent. It suggests that this absorbance can be used for prediction of the ratio of glucose anomers *in vivo*.

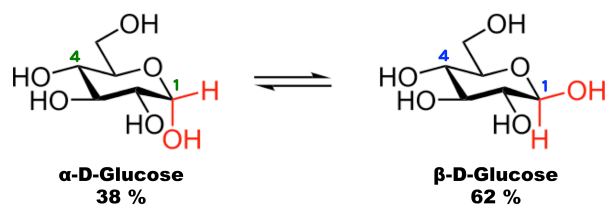


Figure 1. Glucose anomers

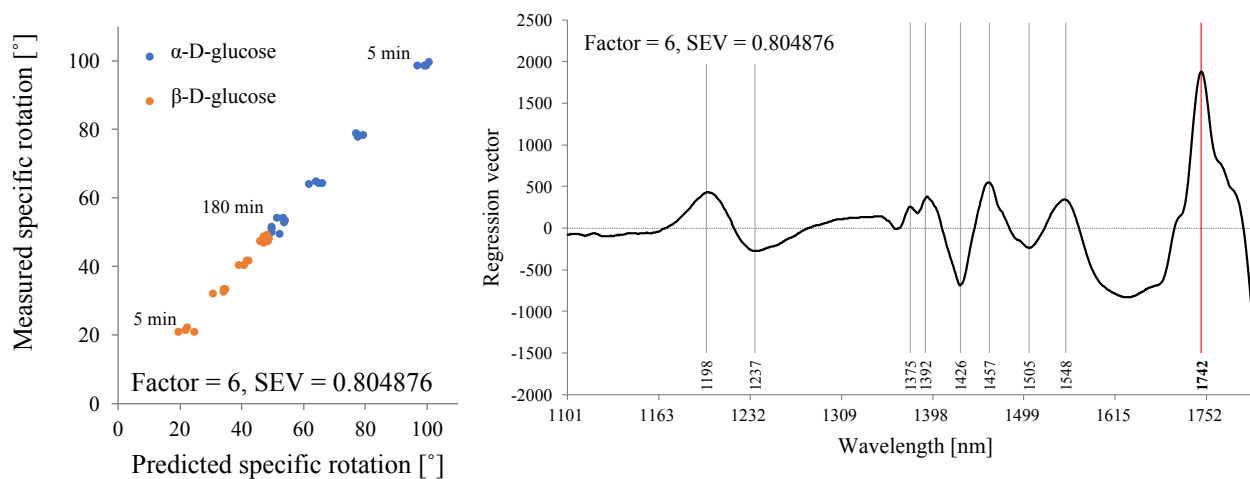


Figure 2. Regression analysis of optical rotation and near-infrared spectra

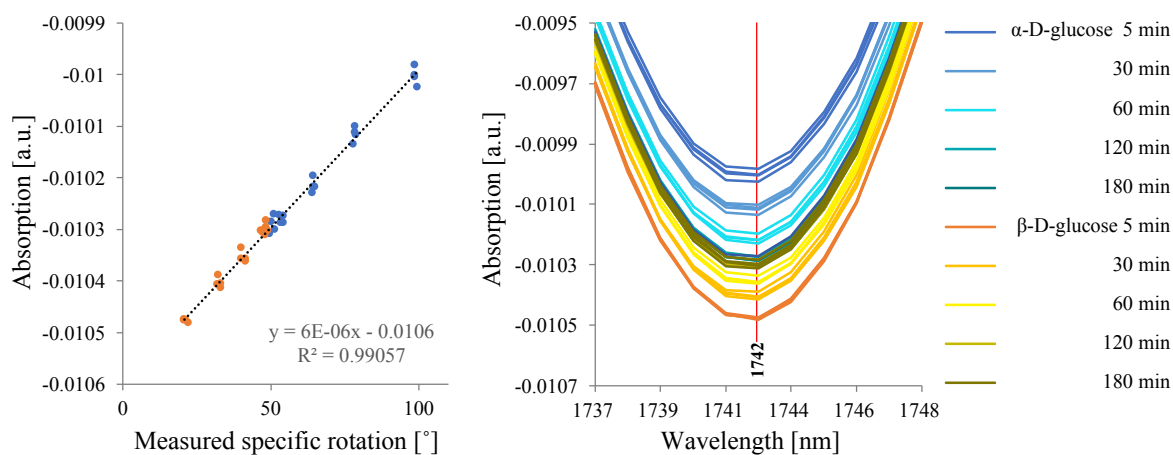


Figure 3. Correlation between optical rotation and absorbance at 1,742 nm

Reference:

Tanaka S., Kojić D., Tsenkova R. and Yasui M., Quantification of anomeric structural changes of glucose solutions using near-infrared spectra. *Carbohydr. Res.*, 463:40-46. 2018,