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# Complete $^{1}H$ and $^{13}C$ NMR spectral assignment of D-glucofuranose

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ABSTRACT

Although D-glucose is the most common sugar in nature, only a few NMR studies have focused on its minor furanose forms, and they have been limited to the anomeric position. Here, complete $^{1}H$ and $^{13}C$ NMR spectral analysis of α- and β-D-glucofuranose was performed, including signal assignment, chemical shifts, and coupling constants. Selective and non-selective 1D and 2D NMR experiments were used for the analysis, complemented by spin simulations and iterative spectral analysis.

## 1. Introduction

D-glucose is a ubiquitous metabolite in biological systems, and is thereby commonly encountered and studied in fields such as carbohydrate chemistry, metabolomics, and food science. Like many other sugars, glucose exists in an equilibrium between different ring forms and open chain tautomers in aqueous solution (Fig. 1). Of these structures, the α- and β-pyranose forms together account for more than 99% of all glucose molecules at ambient temperature, whereas the two furanose forms constitute around 0.3–0.4% and the acyclic aldehyde and hydrate forms around 0.005% each [1,2]. Despite their low abundance, the furanose forms are responsible for about half of the total reactivity of D-glucose, at least at high temperature, due to their fast ring opening rate compared to the pyranose forms [3]. However, in contrast to galactofuranoses, which are frequently found in plant and bacterial polysaccharides [4,5], glucofuranoses are extremely rare as building blocks in biomolecules. A few studies have reported glucofuranose residues from e.g. a bacterial lipopolysaccharide [6] (although this structure might need revision [7]), a plant polysaccharide [8], and as a C-glycosyl derivative from *Aloe barbadensis* [9], but these and other studies with glucofuranose assignments appear to be more or less tentative and so it is still unclear whether glucofuranose is at all present as a component of biomolecules. Furthermore, galactofuranoses are biosynthesized by UDP-galactopyranose mutase [4], but there are no known enzymes that can produce glucofuranoses for incorporation into biomolecules.

The pyranose forms of D-glucose have been extensively studied by NMR spectroscopy [10–14], but the minor forms are less well characterized. The existing studies on the furanose forms have mainly been performed using $^{13}C$ NMR, often with $^{13}C$-labelled glucose, and have focused on the anomeric signals [1,2,15]. To the best of our knowledge, the only $^{1}H$ NMR data published on the glucofuranoses are the values reported for the anomeric protons [3], meaning that no full NMR characterization of these glucose forms has been carried out. This is most likely due to their low abundance and the fact that many of their resonances are obscured by pyranose signals, especially in $^{1}H$ NMR.

In the NMR spectra of dilute glucose solutions, the glucofuranose signals are typically below the limit of detection due to their low intensity compared to the pyranose signals. However, if a sample contains large amounts of glucose and small amounts of other compounds, the concentration of the glucofuranose forms may be comparable to or even higher than that of certain compounds of interest. Such samples may be encountered in e.g. food science, in particular food or beverage quality control, and knowledge about the glucofuranose NMR signals may facilitate the study of low-abundant compounds in these cases. Furthermore, if one is unaware of the glucofuranose NMR chemical shifts and coupling patterns, these signals may erroneously be taken for impurities.

In this work, all $^{1}H$ and $^{13}C$ NMR signals of α- and β-D-glucofuranose in $D_2O$ are characterized for the first time. Signal assignment, chemical shifts, and homo- and heteronuclear coupling constants are reported. The results were obtained using a combination of selective and non-selective 1D and 2D NMR experiments, as well as spin simulations and iterative spectral analysis.

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## 2. Results and discussion

### 2.1. Assignment of the D-glucofuranose NMR signals

When inspecting the $^{1}$H NMR spectrum of D-glucose, minor signals can be observed between 4.07 ppm and 4.32 ppm, i.e. in the area between the signals from the pyranose ring protons and anomeric protons, as well as at 5.49 ppm (Fig. 2a). Additional low-intensity signals, which overlap with glucopyranose signals in the $^{1}$H but not the $^{13}$C dimension, are visible in the corresponding $^{1}$H,$^{13}$C-HSQC spectrum (Fig. 2b). All of the signals have approximately the same intensity, implying that they either belong to the same species or to different species with comparable concentration. Analysis of [1–$^{13}$C]-glucose revealed that the two most downfield of the minor HSQC signals are the H1/C1 atoms of two glucose tautomers (Figure S1) and based on the intensity of the signals relative to the pyranose signals, they most likely belong to the two anomeric forms of glucofuranose. The chemical shifts of the signals also agree well with previously reported NMR data for the glucofuranose anomeric carbons [1,2,15] and protons [3].

To further investigate the observed signals, selective $^{1}$H NMR experiments were performed. Exciting the proton signals at 5.49 ppm, 4.31 ppm, and 4.24 ppm in separate 1D-TOCSY experiments revealed two different spin systems, each containing seven signals (Fig. 3). The signal at 5.49 ppm has previously been assigned to the anomeric proton of α-glucofuranose [3] and has a coupling constant of 3.96 Hz, which is similar to values observed for the anomeric signal of other furanoid 1, 2-*cis* tautomers [16–19]. The other anomeric furanose signal overlaps with the anomeric α-glucopyranose signal in the $^{1}$H NMR spectrum, but is clearly observed in the selective 1D-TOSCY spectrum at 5.21 ppm (Fig. 3C). No splitting can be observed for this signal and a small coupling constant is expected for the anomeric signal of a furanoid 1, 2-*trans* tautomer such as β-glucofuranose [3,16–19]. Adding this to the indications described earlier meant that the NMR signals at 5.49 and 5.21 ppm could be assigned to α- and β-glucofuranose, respectively. The remaining furanose signals were then assigned based on series of selective 1D-TOCSY experiments where the mixing time was varied between 20 and 120 ms (Fig. 3 and S2-S4).

The $^{13}$C resonances were assigned from HSQC spectra based on the $^{1}$H assignments determined above. To observe only the glucofuranoses and to avoid spectral overlap with the pyranose resonances, an f2-band-selective TOCSY-HSQC pulse sequence [20] was employed. In this experiment, a certain part of the $^{1}$H spectrum is excited after which a TOCSY spin-lock restores all signals that are *J*-coupled to any of the excited spins. Connecting this pulse sequence to an HSQC sequence thus enables selected spin systems to be visualized in both the $^{1}$H and the $^{13}$C dimension at the same time. Here, the $^{1}$H spectral region 4.10–4.40 ppm was selectively excited to observe the two glucofuranose spin systems without interference from the pyranose forms (Fig. 4).

### 2.2. Chemical shifts and coupling constants of α- and β-D-glucofuranose

The glucofuranose $^{13}$C NMR chemical shifts are listed in Table 1, together with previously reported $^{13}$C shifts. The chemical shifts were collected from a 1D-$^{13}$C spectrum, apart from α-furanose C2 and β-furanose C5 that were read from an HSQC spectrum due to spectral overlap in the 1D spectrum. To facilitate comparison with previous studies [2,15] the chemical shifts have been referenced to both DSS and TMS, since the $^{13}$C shifts of these reference compounds differ by about 2 ppm [21]. The $^{13}$C chemical shifts agree well with the previously reported data, although the earlier assignments of β-glucofuranose C2 and C4 [15] need to be interchanged. The $^{13}$C chemical shifts are also in close agreement with those of the corresponding methyl glucofuranosides [22], apart from the C1 resonances that are affected by the methyl group in the methyl furanosides (Table 1). One-bond $^{13}$C–$^{1}$H coupling constants, also listed in Table 1, were determined from an f2-band-selective TOCSY-HSQC spectrum recorded without carbon decoupling. A previous study on methyl furanosides found that the $J_{C1,H1}$ is 174.0 Hz for methyl α-glucofuranoside and 172.5 Hz for methyl

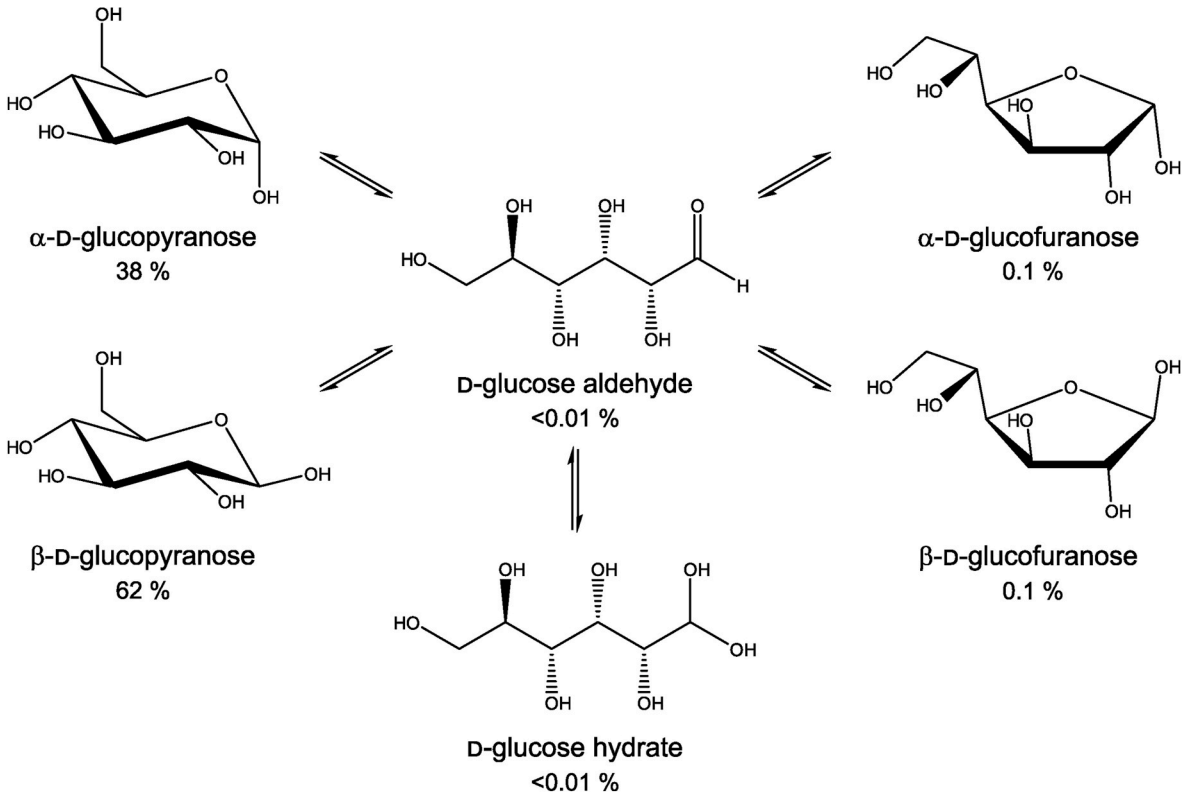


**Fig. 1.** The anomeric equilibrium of D-glucose in aqueous solution, with relative abundances at 25 °C and pD 7.

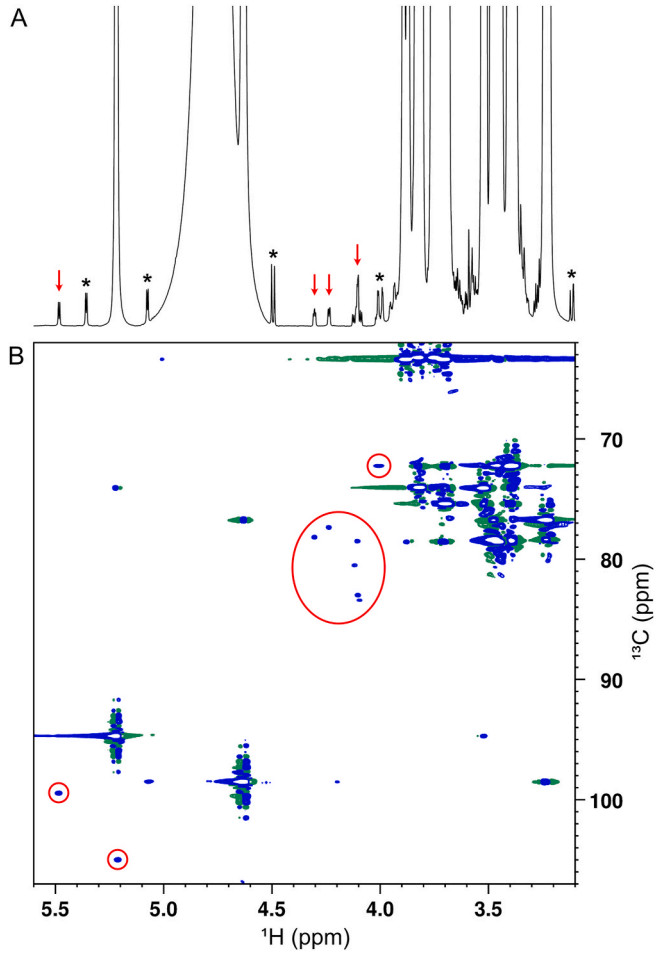


**Fig. 2.** A) 1D $^{1}$H NMR spectrum of D-glucose in $D_2O$ at 25 °C. The arrows denote minor signals not corresponding to $^{13}$C satellites of the glucopyranose signals (indicated with asterisks). B) $^{1}$H,$^{13}$C-HSQC spectrum of D-glucose in $D_2O$ (25 °C), with the minor signals encircled.

β-glucofuranoside [23], which is very close to what was found here for the free furanoses.

Spin simulations and iterative spectral analysis were performed to verify the glucofuranose $^{1}$H chemical shifts and to determine homonuclear two- and three-bond $^{1}$H coupling constants (Table 2 and Fig. 5). Non-selective 1D-$^{1}$H spectra were used as input for the simulations when possible, however the signals of α- and β-furanose H5, H6a, and H6b, as well as β-furanose H1, are covered by pyranose signals and therefore selective 1D-$^{1}$H spectra were used to analyse these signals (see Figure S5). Because selective spectra can suffer from distortions in signal shape and intensity, zero-quantum coherence suppression was used to minimize anti-phase components; however the accuracy of the extracted coupling constants may still be compromised. Furthermore, the $J_{H1,H2}$ and $J_{H2,H3}$ of the β anomer are both around 1 Hz in size and difficult to determine with high accuracy because of broad, overlapping signals. Long-range $^{1}$H–$^{1}$H coupling constants have earlier been observed for the pyranose form of α-D-glucose [12] and are likely to be present in the furanose forms as well. However, no long-range couplings were resolved

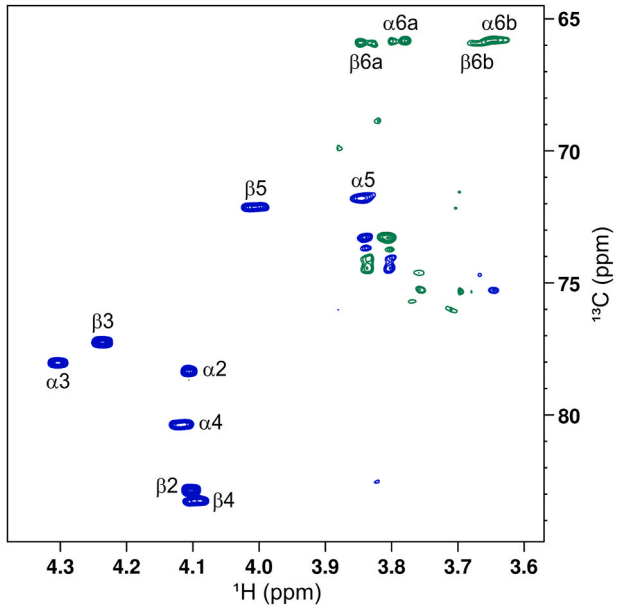


**Fig. 4.** Multiplicity-edited f2-band-selective $^{1}$H,$^{13}$C-HSQC spectrum of D-glucose in $D_2O$ (25 °C) with assignment of the glucofuranose ring signals. Non-assigned cross-peaks are mainly from residual pyranose signals.

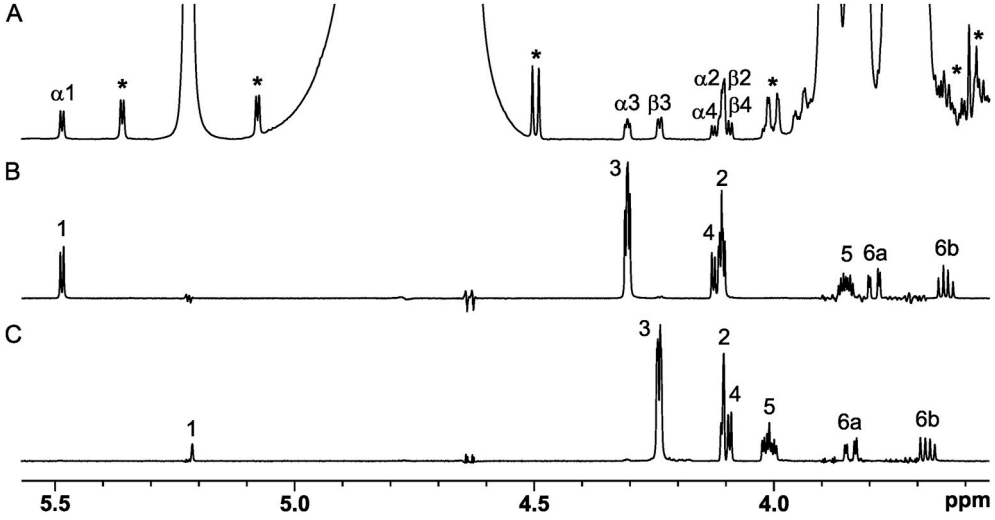


**Fig. 3.** Assignment of the D-glucofuranose $^{1}$H NMR signals. A) 1D-$^{1}$H NMR spectrum of D-glucose with the furanose signals indicated. Glucopyranose $^{13}$C satellites are marked with asterisks. B) Selective 1D-TOCSY spectrum of α-glucofuranose obtained by exciting the H3 signal at 4.30 ppm. C) Selective 1D-TOCSY spectrum of β-glucofuranose obtained by exciting the H3 signal at 4.24 ppm. The mixing time was 100 ms in both B) and C).

**Table 1**
$^{13}$C NMR chemical shifts ($\delta$, ppm) and $^{1}J_{C,H}$ coupling constants (Hz) of α- and β-D-glucofuranose in $D_2O$ (25 °C, pD 7.0). Results from previous studies (in parentheses) are included as reference.

| | | C1 | C2 | C3 | C4 | C5 | C6 |
|---|---|---|---|---|---|---|---|
| α | $\delta_{DSS}$ | 99.43 | 78.49[a] | 78.16 | 80.51 | 71.92 | 65.95 |
| | $\delta_{TMS}$ | 97.64 | 76.69[a] | 76.36 | 78.71 | 70.12 | 64.15 |
| | $^{1}J_{C,H}$[b] | 172.6 | 152.6 | 153.1 | 146.3 | n.d.[c] | 143.3 (6a)<br>142.7 (6b) |
| | $\delta_{TMS}$[d] [2] | (97.6) | - | - | - | - | - |
| | $\delta_{TMS}$[e] [22] | (104.0) | (77.7) | (76.6) | (78.8) | (70.7) | (64.2) |
| β | $\delta_{DSS}$ | 104.98 | 82.98 | 77.38 | 83.40 | 72.27[a] | 66.08 |
| | $\delta_{TMS}$ | 103.18 | 81.18 | 75.58 | 81.60 | 70.47[a] | 64.28 |
| | $^{1}J_{C,H}$[b] | 172.7 | 154.5 | 153.1 | 147.8 | 146.8 | 143.3 (6a)<br>142.7 (6b) |
| | $\delta_{TMS}$[f] [15] | (103.8) | (82.1) | - | (81.8) | - | - |
| | $\delta_{TMS}$[d] [2] | (103.2) | - | - | - | - | - |
| | $\delta_{TMS}$[e] [22] | (110.0) | (80.6) | (75.8) | (82.3) | (70.7) | (64.7) |

[a] The chemical shift was determined from an HSQC spectrum, with an uncertainty of around 0.01 ppm.
[b] The standard error was estimated to 0.1 Hz, except for the C6/H6 couplings where the error was estimated to 0.5 Hz.
[c] Not determined.
[d] Externally referenced to the chemical shift of C1 in α-D-[1–$^{13}$C]mannopyranose (95.0 ppm). Recorded at 30 °C.
[e] Methyl glucofuranoside.
[f] Recorded at 41 °C.

**Table 2**
$^{1}$H NMR chemical shifts ($\delta$, ppm) and $J_{H,H}$ coupling constants (Hz) of α- and β-D-glucofuranose in $D_2O$ (25 °C, pD 7.0).

| | | H1 | H2 | H3 | H4 | H5 | H6a | H6b |
|---|---|---|---|---|---|---|---|---|
| α | $\delta_{DSS}$ | 5.486 | 4.108 | 4.306 | 4.119 | 3.850 | 3.790 | 3.642 |
| | $J_{H,H}$[a] | $^{3}J_{1,2}$ = 3.96 | $^{3}J_{2,3}$ = 2.42 | $^{3}J_{3,4}$ = 3.85 | $^{3}J_{4,5}$ = 8.50 | $^{3}J_{5,6a}$ = 2.87<br>$^{3}J_{5,6b}$ = 6.22 | $^{2}J_{6a,6b}$ = 12.00 | = (−) |
| β | $\delta_{DSS}$ | 5.213 | 4.104 | 4.238 | 4.098 | 4.009 | 3.838 | 3.679 |
| | $J_{H,H}$[a] | $^{3}J_{1,2}$ < 1 | $^{3}J_{2,3}$ ≈ 1.2 | $^{3}J_{3,4}$ = 4.19 | $^{3}J_{4,5}$ = 9.00 | $^{3}J_{5,6a}$ = 2.75<br>$^{3}J_{5,6b}$ = 6.05 | $^{2}J_{6a,6b}$ = 11.99 | = (−) |

[a] Standard errors are 0.05 Hz or less, except for α-furanose $^{3}J_{5,6a}$ that has an uncertainty of 0.1 Hz.

in the spectra, indicating that they are probably small in size. Comparing the coupling constants with previous data shows good agreement; Kaufmann et al. [3] reported that α- and β-glucofuranose $J_{H1,H2}$ are 3.9 Hz and "less than 1 Hz", respectively, whereas the corresponding methyl glucofuranoside coupling constants are 4.2 Hz and 1.0 Hz, respectively [19]. Here, 3.96 Hz and <1 Hz were found for the α- and β-glucofuranose $J_{H1,H2}$, respectively.

The ring-opening rate of glucofuranose is about 1 $s^{-1}$ at 87 °C [3], which is much faster than that of the pyranose forms (0.004–0.008 $s^{-1}$ at 87 °C [3] or 0.001–0.002 $s^{-1}$ at 30 °C [24]). Chemical exchange can affect NMR spectra so that signals are broadened or observed as an average between the two exchanging species, but in the case of glucofuranose at room temperature no such signal broadening was observed. Hence, the ring-opening of the glucofuranose ring is slow on the NMR timescale and the reported chemical shifts are thus not considered to be affected by chemical exchange.

### 2.3. Relative quantification of the D-glucopyranose and furanose anomers

To determine the relative amounts of the different D-glucose anomers at 25 °C and pD 7.0, a 1D-$^{1}$H NMR spectrum was recorded with a long relaxation delay (>5 × $T_1$). The α-pyranose was found to account for 37.5% and the β-pyranose for 62.2% of the total glucose, which is within the previously reported α/β ratio [1,2,12,13,15], whereas α-furanose made up 0.12% and β-furanose 0.13%. A similar result was obtained using quantitative $^{13}$C NMR on [1–$^{13}$C]-glucose: 37.5% α-pyranose, 62.3% β-pyranose, and 0.11–0.12% of each furanose form. It should be noted that the anomeric signals were used for quantification in $^{13}$C NMR, but other signals had to be used in $^{1}$H NMR since the α-pyranose and β-furanose anomeric signals overlap with each other and the anomeric β-pyranose signal overlaps with the residual water signal (see section 4.2 for details). For quantitative purposes, $^{1}$H NMR is the preferred choice in order to minimize the effects of the longer relaxation times of $^{13}$C that require long recovery delays. Furthermore, the signal to noise ratio is often better in $^{1}$H NMR spectra, making the integration more reliable especially when dealing with low-intensity signals as in this case. The results from previous studies are somewhat disparate. One study found that the α- and β-furanose, at 27 °C and pH 4.7, constitute 0.14% and 0.15%, respectively [1], which is very similar to the results obtained here. Another study, performed at 30 °C, found that the amount of α-furanose is significantly lower than that of β-furanose: 0.108% and 0.28%, respectively [2]. Both these studies quantified the anomers using $^{13}$C NMR on [1–$^{13}$C]-glucose. It is known that the anomeric equilibrium of sugars is affected by factors such as sugar concentration [13,15],

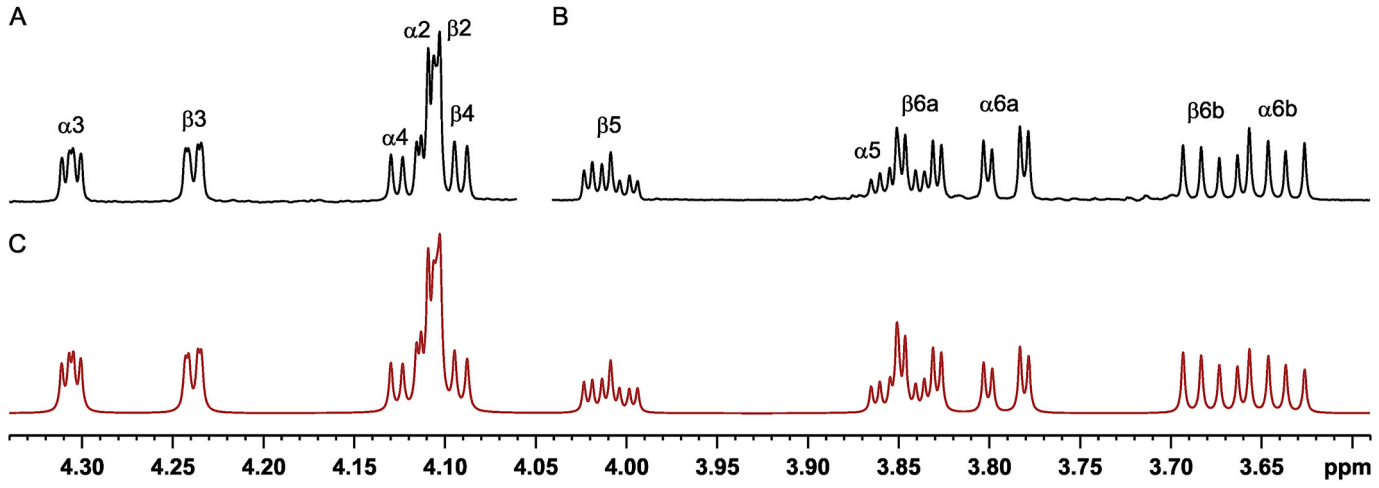


**Fig. 5.** Experimental (A and B) and calculated (C) $^{1}$H NMR spectra of the glucofuranose ring protons. Due to spectral overlap with the pyranose forms in the right part of the $^{1}$H NMR spectrum, A) is a standard 1D spectrum whereas B) is a 1D-TOCSY spectrum obtained by band-selective excitation of the spectral region 4.10-4.40 ppm. See also Figure S5-S7.

temperature [1], pH, and buffer concentration [25,26], which may explain some of the discrepancy. Here, the glucose concentration was 1 M and a dilute phosphate buffer was used to keep the pD at 7.0.

## 3. Conclusions

In this study, the complete $^{1}H$ and $^{13}C$ NMR chemical shifts of both D-glucofuranose anomers are reported for the first time. This new knowledge can be utilized e.g. when studying glucofuranose conformation and glucose ring-chain tautomerism. Furthermore, although the furanoses constitute less than 1% of the total glucose, knowing their chemical shifts can be essential for studies of low-abundant compounds in solutions containing high amounts of glucose, where some of the furanose signals may interfere with the signals of interest. This study also highlights the usefulness of selective and band-selective NMR experiments for characterization of low-abundant compounds when other compounds in high concentration cause spectral interference.

## 4. Experimental

### 4.1. General methods

Anhydrous D(+)-glucose was purchased from VWR. [1–$^{13}C$]-glucose was purchased from Cambridge Isotope Laboratories, Inc. Glucose solutions (1 M) were prepared using 20 mM $KH_2PO_4$ buffer in $D_2O$, pD 7.0 (apparent pH 6.6), as solvent. DSS-$d_6$ (sodium 3-(trimethylsilyl)propane-1-sulfonate-$d_6$) was added as a chemical shift reference in a concentration of approximately 5 mM. To some of the samples, TMS (tetramethylsilane) was added as well. The solutions were equilibrated in room temperature for at least 24 h prior to NMR analysis. Before NMR acquisition, the pD was checked again and adjusted to 7.0 using NaOH dissolved in $D_2O$ if necessary.

### 4.2. NMR spectroscopy

NMR analysis was performed on a Bruker Avance III 600 MHz spectrometer with a 5 mm $^{1}H/^{13}C/^{15}N/^{31}P$ inverse detection cryoprobe or a 5 mm broadband observe detection SmartProbe, both equipped with a z gradient. Spectra were recorded at 25 °C and were processed with TopSpin 4.0.6. The spectrometer temperature was calibrated in connection to the experiments using 4% methanol in methanol-$d_4$. The carrier frequency was placed on the HDO signal (4.70 ppm). SUN (Suppression of UNwanted signals) pulse sequences [20] (1D-$^{1}H$, $^{1}H$,$^{1}H$-TOCSY, and $^{1}H$,$^{13}C$-HSQC) were used for selective excitation experiments. As the 180° selective excitation pulse, either an IBURP-2 (25.8 ms) or a Gaussian pulse (80 ms) was used depending on the width of the selected area; when only one spin was excited the latter pulse was employed due to its narrower excitation profile. The TOCSY spin-lock was 100 ms if not stated otherwise. For quantitative $^{1}H$ NMR, a relaxation delay of 20 s (including the acquisition time) was used and the following signals were integrated: α-pyranose H1 or H2, β-pyranose H2 or H6a, α-furanose H1 or H3, and β-furanose H3. For quantitative 1D $^{13}C$ NMR, the inverse-gated decoupled Bruker pulse sequence *zgig30* was used, with a relaxation delay of 40 s. Before quantitation, spectral baseline points were defined after which the baseline was corrected using cubic spline. The number of data points collected in HSQC was 1024 or 2048, apart from the HSQC without decoupling where 8192 data points were collected.

### 4.3. Spin simulations

Spin simulations and iterative spectral analysis were performed using the Daisy module in TopSpin. Proton chemical shifts and coupling constants that could be extracted directly from the spectra (both selective and non-selective) were used as starting values for the simulations. Thereafter, the *J*-value, chemical shift, and line width for each spin were iterated until the best possible fit was achieved, judged by visual evaluation.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.carres.2021.108477.

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