

**Supplementary information for**  
***Ultrafast high-resolution magic-angle spinning NMR spectroscopy***

Marion André,<sup>a</sup> Martial Piotto,<sup>b,c</sup> Stefano Caldarelli<sup>a,d</sup> and Jean-Nicolas Dumez<sup>a</sup>

<sup>a</sup>*Institut de Chimie des Substances Naturelles, CNRS UPR 2301, Avenue de la Terrasse 91190  
Gif-sur-Yvette, France*

<sup>b</sup>*Bruker Biospin, Laboratoire d'applications RMN, 34 rue de l'industrie  
67166 Wissembourg, France*

<sup>c</sup>*Strasbourg University, IMIS/ICube Laboratory, 67000 Strasbourg, France*

<sup>d</sup>*Aix Marseille Université, Centrale Marseille, CNRS, iSm2 UMR 7313,  
13397 Marseille, France*

Materials and Methods p. 2

Supplementary figures p. 5

## Materials and Methods

### *Sample preparation*

Solutions of individual sugars were prepared at a 0.5 M concentration by dissolving 85 mg, 45 mg and 45 mg of anhydrous sucrose, glucose and fructose (Sigma Aldrich, analytical quality) respectively in 0.5 mL of D<sub>2</sub>O. Disposable inserts with a volume of 33  $\mu$ L (Bruker) were filled with the solutions, taking care that no air bubble was present into the sample.

The banana sample was prepared by placing approximately 10 mg of fresh banana into a disposable insert. Centrifugation (15 s, 7000 rpm) was used to help the sample fit in the insert cavity. The remaining volume of the insert was carefully filled with D<sub>2</sub>O.

The water sample was prepared by filling a disposable insert with D<sub>2</sub>O.

The inserts were placed into regular 4 mm o.d., 96  $\mu$ L HR-MAS rotors (Bruker) for analysis.

### *NMR spectroscopy*

All NMR experiments were performed at room temperature on a Bruker Avance I spectrometer operating at a <sup>1</sup>H Larmor frequency of 600.13 MHz and equipped with a 4-mm double resonance (<sup>1</sup>H, <sup>13</sup>C) gradient HR-MAS probe.

The ultrafast single-scan COSY spectrum of sucrose was recorded using the scheme of Fig. 1a of the main text, with Chirp pulses of a duration of 15 ms and a sweep range of 8 kHz for spatial encoding. The amplitudes of the spatial encoding gradients and coherence selection gradients were 2.16 G/cm, and 32.4 G/cm, respectively. 54 gradients pairs were used during acquisition, each one lasting 780.8  $\mu$ s with an amplitude of 27 G/cm. This corresponds to a spectral width of 640 Hz in the conventional dimension and 1272 Hz in the ultrafast dimension. Presaturation during 2.5 s was used for water suppression, leading to an overall experimental time of less than 3 s.

Ultrafast DQS spectra of the 0.5M solution of sucrose were recorded using the scheme of Fig. 2a of the main text, with the same parameters, except for the coherence selection gradients for mixing which were set to 21.6 G/cm and 43.2 G/cm before and after the mixing pulse, respectively. The single-scan DQS spectrum was recorded in less than 3 s. For the interleaved spectrum, 2 interleaves were recorded to double the spectral width in the

conventional dimension, with a delay of 2.5s between scans. Presaturation was used during this delay for water suppression. Four dummy scans were added as well as purge gradients between scans in order to suppress any residual magnetisation. The total duration for the interleaved spectrum was 16 s.

In the optimal conditions, the spinning frequency was  $\nu_r = 3.84$  kHz, which is 6 times the spectral width in the conventional dimension and corresponds to a rotor period of  $T_r = 260$   $\mu$ s. Destructive interferences were observed if the spinning frequency was set to  $\nu_r = 4.48$  kHz, which corresponds to 7 times the spectral width in the conventional dimension and corresponds to a rotor period of  $T_r = 223$   $\mu$ s.

The ultrafast DQS spectrum of the banana sample was recorded with the same parameters used for sucrose in terms of spatial encoding and coherence selection. During the acquisition, 46 gradients pairs were used, each one lasting 896  $\mu$ s with an amplitude of 27 G/cm. Three interleaves were used, with four scans each; 4 dummy scans were also added. An inter-scan delay of 5 s was used, resulting a total duration of 1 m 23 s. Presaturation was used during the relaxation delay for water suppression. These parameters result in a spectral width of 1674 Hz in the conventional dimension and 1440 Hz in the ultrafast dimension. The spinning frequency was  $\nu_r = 4.46$  kHz, which is 8 times the spectral width in the conventional dimension if no interleaving is used and corresponds to a rotor period of  $T_r = 224$   $\mu$ s.

Conventional DQS spectra of sucrose, glucose, fructose and fresh banana were recorded at a spinning rate of 4 kHz with 512  $t_1$  increments and 1 scan, with an inter-scan delay of 2.5 s, during which presaturation was applied for water suppression. The spectral width was 6 ppm in both dimensions of the DQS spectrum for a total acquisition time of 27 min and 23 sec. The spectra were processed in magnitude mode with a squared sinebell weighting function in both dimensions.

In both ultrafast and conventional DQS experiments, the final (mixing) pulse had a flip angle of  $120^\circ$  in order to maximize the sensitivity for direct peaks. The buildup time for multi-spin coherences was set to 16.6 ms.

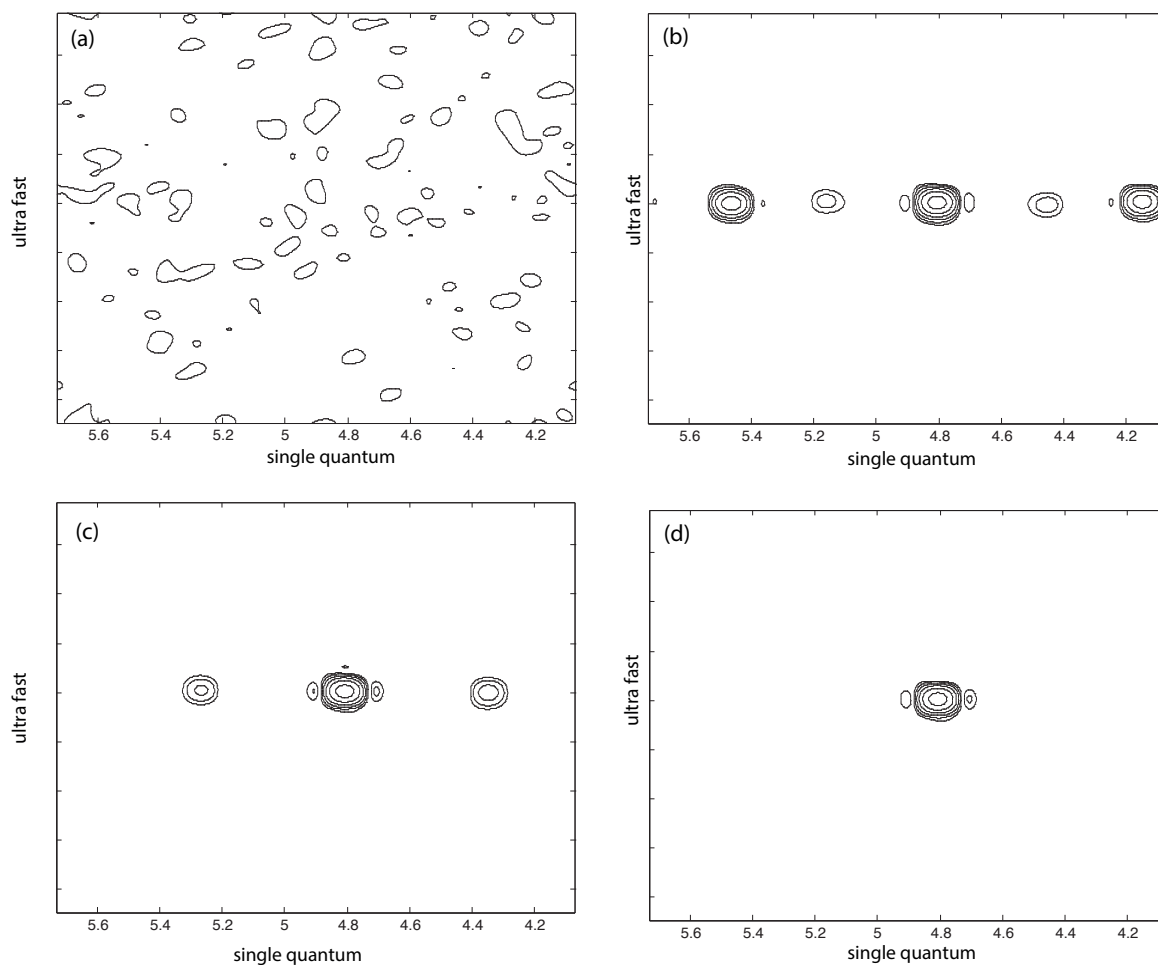
EPSI data of water were recorded using 32 gradients pairs, each one lasting 500  $\mu$ s with an amplitude of 27 G/cm. In the optimal conditions, the spinning frequency was  $\nu_r = 4$  kHz, which is 4 times the spectral width in the conventional dimension and corresponds to a

rotor period of  $T_r = 250 \mu\text{s}$ . Destructive interferences were observed if the spinning frequency was  $\nu_r = 3 \text{ kHz}$ , which is 3 times the spectral width in the conventional dimension and corresponds to a rotor period of  $T_r = 333 \mu\text{s}$ . Non-folded spinning sidebands were observed if the spinning frequency was  $\nu_r = 400 \text{ Hz}$ , which corresponds to a rotor period of  $T_r = 2.5 \text{ ms}$ . Folded spinning sidebands were observed if the spinning frequency was  $\nu_r = 3.28 \text{ kHz}$ , which corresponds to a rotor period of  $T_r = 305 \mu\text{s}$ .

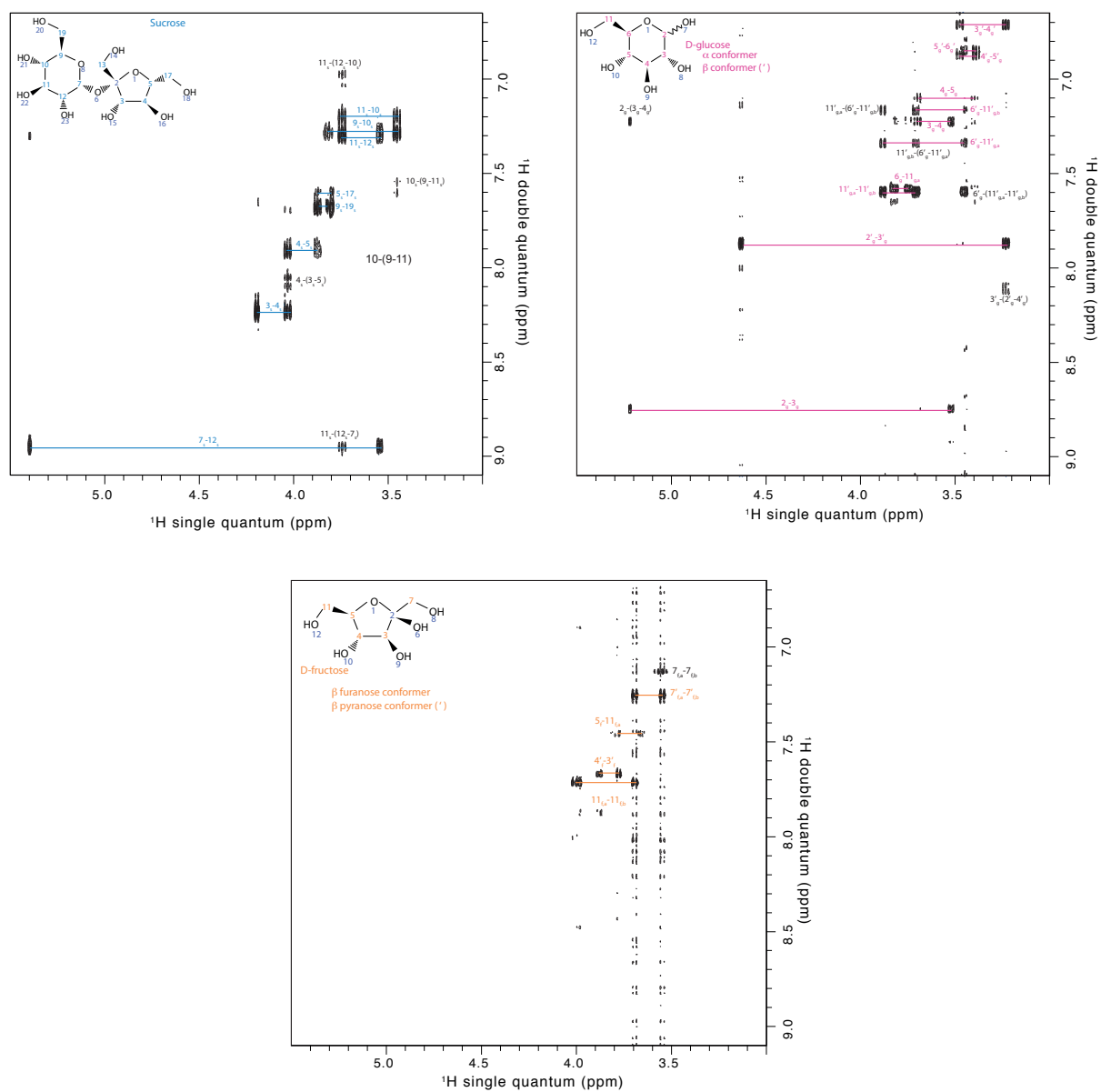
Processing of ultrafast spectra was done using an optimised Gaussian weighting function in the ultrafast dimension and a sinebell weighting function in the conventional dimension, using a home-written routine in Matlab.

Assignments of the signals were made with the help of the Human Metabolome DataBase ([www.hmdb.ca](http://www.hmdb.ca)).

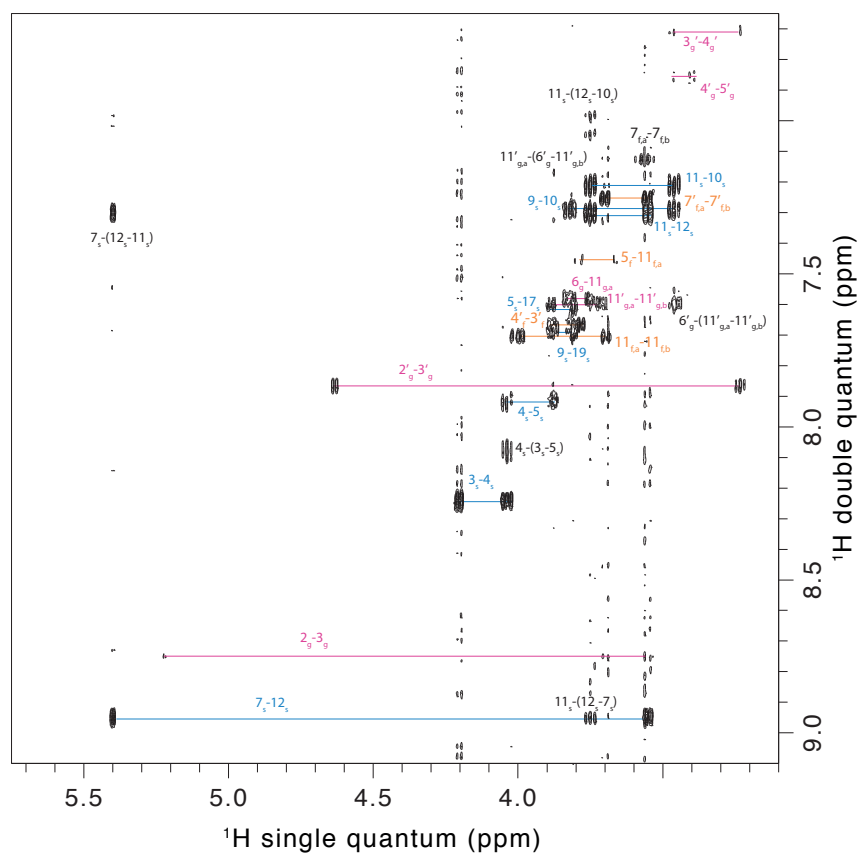
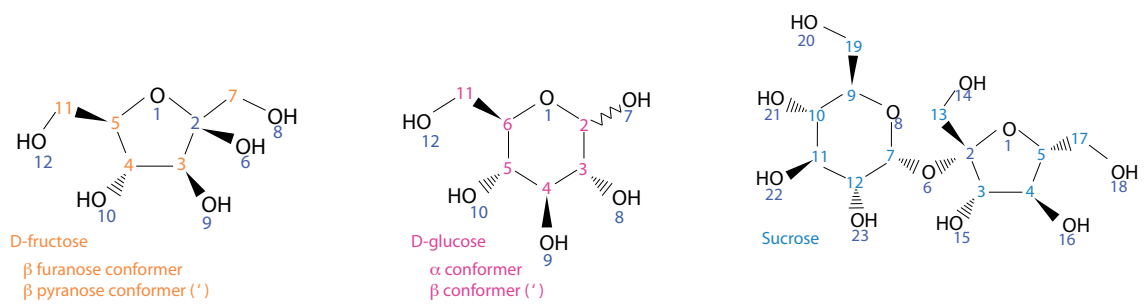
## Supplementary figures



**Fig. S1.** 2D spectra obtained with an EPSI acquisition on a sample of  $D_2O$  (the residual protonated water peak is observed), using a HR-MAS setup. The data are Fourier transformed in the time dimension only. The readout gradients have a duration  $T_a = 500 \mu s$ . The spinning frequency is adjusted to show (a) destructive interference ( $\nu_r = 3$  kHz); (b) non-folded spinning sidebands ( $\nu_r = 400$  Hz); (c) folded spinning sidebands ( $\nu_r = 3.28$  Hz) and (d) no spinning sidebands ( $\nu_r = 4$  kHz).



**Fig. S2.** Conventional DQS spectra of the sugar region for 0.5 M solutions of (a) sucrose, (b) glucose and (c) fructose in D<sub>2</sub>O, obtained with a HR-MAS setup.



**Fig. S3.** Conventional DQS spectrum of the sugar region for a sample of fresh banana; obtained with a HR-MAS setup.