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Supporting Information

Aromatic – Carbohydrate Interactions: an NMR and Computational Study of Model Systems

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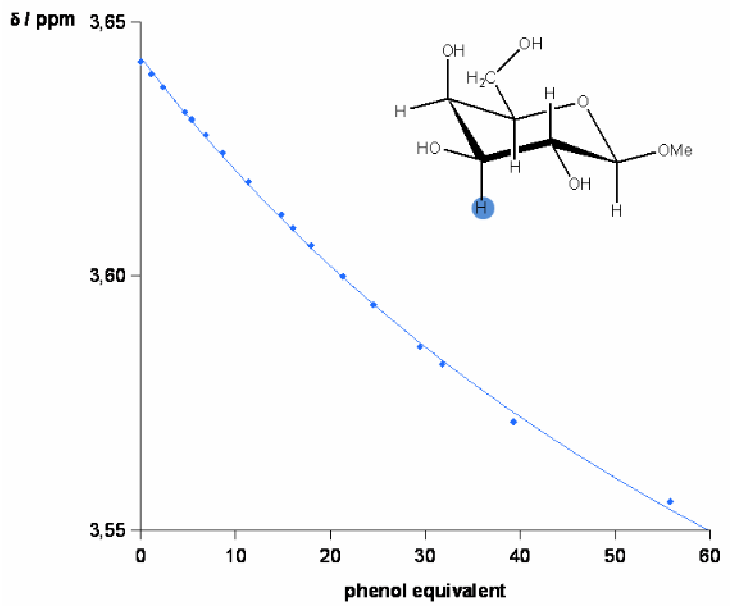

Figure S1 Variation of the chemical shift of 10 mM methyl β-D-galactopyranoside H3 upon phenol titration. The curve represents the parametric adjustment using a non linear fitting to the experimental data (1:1 interaction model; fast exchange at the NMR chemical shift timescale which leads to the observation of the average between the chemical shift of the free sugar and the complexed sugar). The affinity constant obtained by the fitting is 1 M^{-1}.

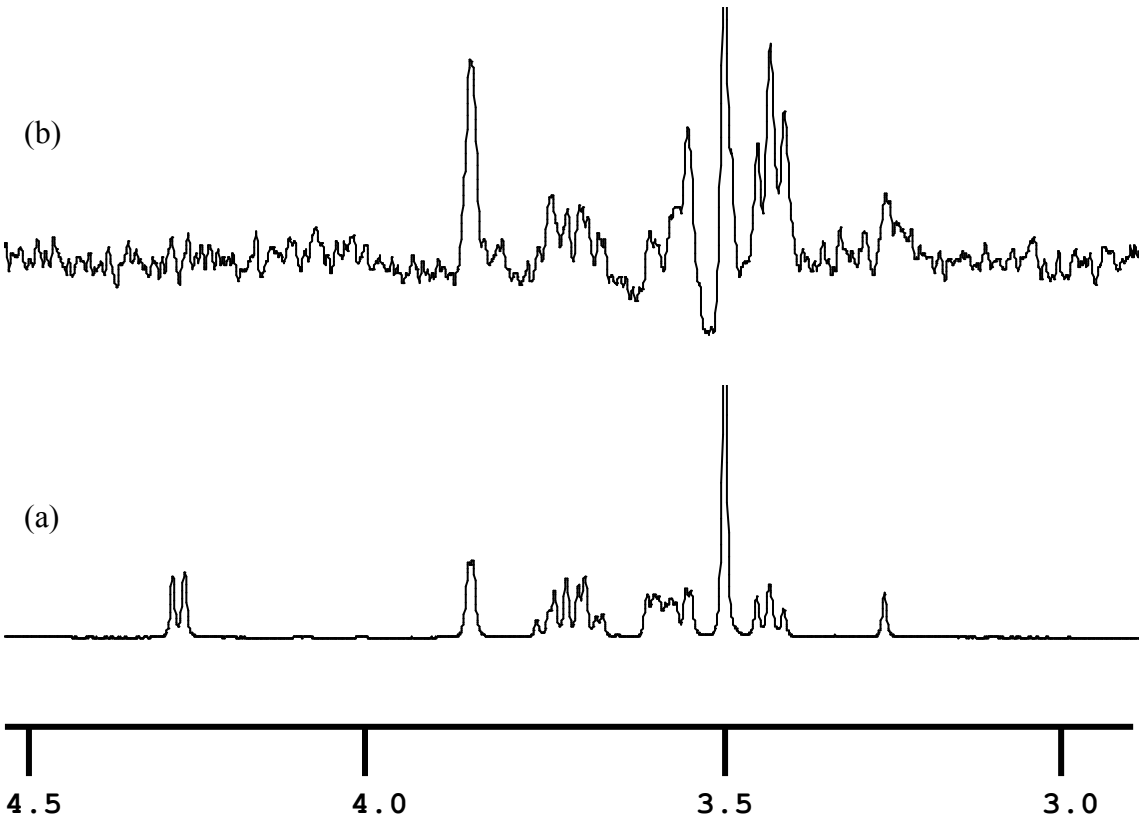

Figure S2. 1D ^{1}H spectrum of methyl β-galactopyranoside (a) and (b) the experimental homonuclear NOE spectrum recorded after selective irradiation of the water signal. The NOE experiment was recorded using the DPFGSE-NOE sequence with a 0.8 s of mixing time, a relaxation delay of 2.5 s and 1024 transients. For both spectra, standard 1D processing with exponential multiplication (lb=1 Hz) was used.

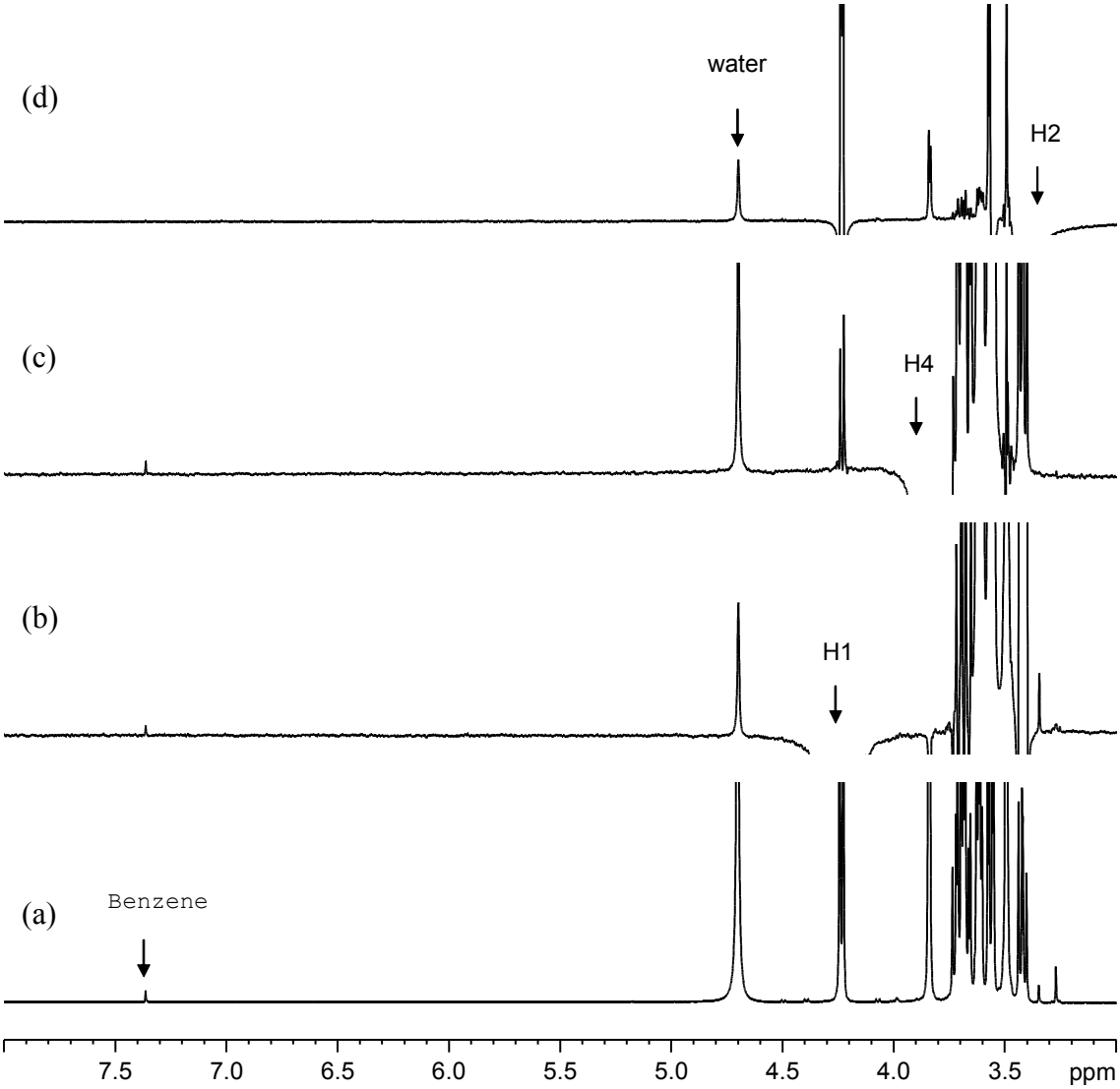

Figure S3. 1D ^{1}H spectrum of methyl β-galactopyranoside (a) and the experimental homonuclear NOE spectra recorded after selective irradiation of protons H1 (b), H4 (c) and H2 (d) of methyl β-galactopyranoside. All experiments were recorded using a standard selnogp sequence (Bruker Avance). The 180° selective pulses (i.e. 50 or 70ms of duration and 63 or 72 dB of transmitter frequency respectively) were adjusted to the sugar signals. All spectra in the figure were recorded using a 1s mixing time and a relaxation delay of 8s and 64 transients. For each experiment, standard 1D processing with exponential multiplication (lb=1 Hz) was used.

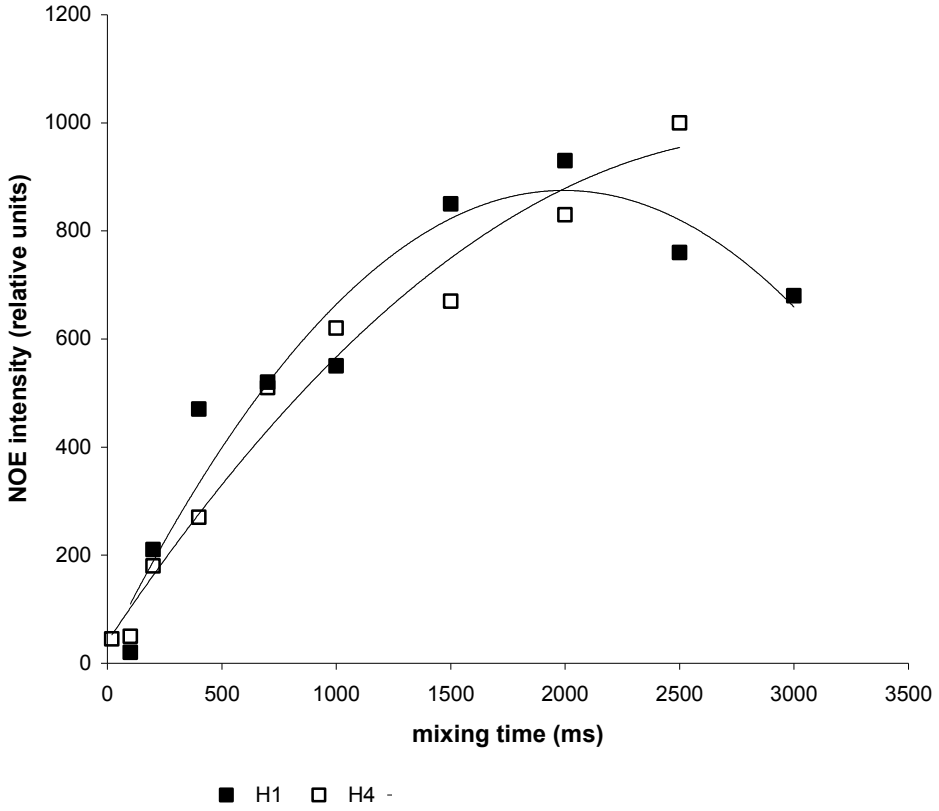

Figure S4. Build up curve of the experimental intermolecular homonuclear NOE enhancement between H1 (filled squares) or H4 (empty squares) of methyl β-galactopyranoside (inverted signal, 400mM) and the benzene signal (ca 22mM) in water.

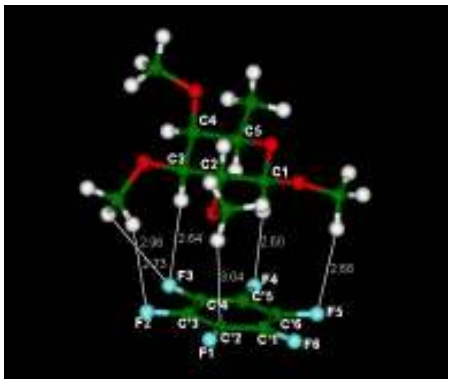

Figure S5. Stationary States of the supramolecules composed by $FucMe_4/C_6F_6$. No CH-π interaction takes place, since the sugar is shifted from the centre of the ring. In this place, the interaction between both molecules is mediated by C-H…F contacts.

Supporting information

Synthesis of the two anomers of O-methyl D-ribofuranoside:

All chemicals were purchased from Sigma, Aldrich or Fluka and were used without further purification. Powdered D-ribose (2g) was heated during 48h at 40°C in methanol (20ml) in presence of anhydrous cupric sulphate (4g) containing a catalytic amount of sulphuric acid (70µl), under argon atmosphere. The solution was then neutralized by the addition of lead bicarbonate, filtered through cotton and washed with acetone. The solvents were evaporated under reduced pressure. Per-O-acetylation of the mixture of methyl ribosides was performed by reaction with pyridine (30ml) and acetic anhydride (15ml), under argon atmosphere at 0°C during 36h. The reaction mixture was poured onto ice. The products were then extracted by dichloromethane. The extract was washed with sodium bicarbonate, then with saturated sodium chloride, dried over magnesium sulfate, and filtered through cotton. The solvents were evaporated under reduced pressure. The products were separated by « flash » chromatography on silica gel (Kieselgel Si 60, 40–63 µm) with cyclohexane/ethyl acetate 3:1 as eluent. The separated per-O-acetylated compounds (α-ribofuranoside: 850 mg; β-ribofuranoside: 1,3g) were then characterized by NMR. The α-ribofuranoside (400mg) was deacetylated by dissolving it in methanol (50ml) in the presence of potassium carbonate (165mg). The β-ribofuranoside (200mg) was deacetylated by dissolving it in methanol (50ml) in the presence of potassium carbonate (80mg). The corresponding solutions were then filtered through silica and concentrated to yield the pure target O-methyl α- and β-D-ribofuranosides, which were characterized by NMR.

per-O-acetylated α-ribofuranoside

^{1}H-NMR (600MHz, $CDCl_3$) δ=5.135 (1H, d, J_{1-2}=4.4Hz, H1), 4.969 (1H, dd, J_{1-2}=4.4Hz, J_{2-3}=7.5Hz, H2), 5.167 (1H, dd, J_{2-3}=7.5Hz, J_{3-4}=3.6Hz, H3), 4.277 (1H, ddd, J_{3-4}=3.6Hz, J_{4-5a}=2.8Hz, J_{4-5b}=4.1Hz, H4), 4.394 (1H, dd, J_{4-5a}=2.8Hz, J_{5a-5b}=12.0Hz, H5a), 4.220 (1H, dd, J_{4-5b}=4.1Hz, J_{5a-5b}=12.0Hz, H5b), 3.446 (3H, s, OAc), 2.147 (3H, s, OAc), 2.143 (3H, s, OAc), 2.105 (3H, s, OAc)

per-O-acetylated β-ribofuranoside

^{1}H-NMR (600MHz, $CDCl_3$) δ=4.899 (1H, d, J_{1-2}≈0Hz, H1), 5.218 (1H, dd, J_{1-2}≈0Hz, J_{2-3}=4.7Hz, H2), 5.323 (1H, dd, J_{2-3}=4.7Hz, J_{3-4}=7.0Hz, H3), 4.303 (1H, ddd, J_{3-4}=7.0Hz, J_{4-5a}=3.5Hz, J_{4-5b}=5.9Hz, H4), 4.369 (1H, dd, J_{4-5a}=3.5Hz, J_{5a-5b}=11.7Hz, H5a), 4.044 (1H, dd, J_{4-5b}=5.9Hz, J_{5a-5b}=11.7Hz, H5b), 3.372

(3H, s, OAc), 2.115 (3H, s, OAc), 2.102 (3H, s, OAc), 2.060 (3H, s, OAc)

O-methyl α-ribofuranoside

^{1}H-NMR (600MHz, D_2O) δ=3.430 (3H, s, OMe), 4.995 (1H, d, J_{1-2}=4.4Hz, H1), 4.116 (1H, dd, J_{1-2}=4.4Hz, J_{2-3}=6.3Hz, H2), 4.036 (1H, dd, J_{2-3}=6.3Hz, J_{3-4}=3.5Hz, H3), 4.099 (1H, ddd, J_{3-4}=3.5Hz, J_{4-5a}=3.4Hz, J_{4-5b}=4.6Hz, H4), 3.738 (1H, dd, J_{4-5a}=3.4Hz, J_{5a-5b}=12.4Hz, H5a), 3.663 (1H, dd, J_{4-5b}=4.6Hz, J_{5a-5b}=12.4Hz, H5b)

O-methyl β-ribofuranoside

^{1}H-NMR (600MHz, D_2O) δ=3.397 (3H, s, OMe), 4.898 (1H, d, J_{1-2}=1.3Hz, H1), 4.032 (1H, dd, J_{1-2}=1.3Hz, J_{2-3}=4.8Hz, H2), 4.155 (1H, dd, J_{2-3}=4.8Hz, J_{3-4}=7.0Hz, H3), 4.009 (1H, ddd, J_{3-4}=7.0Hz, J_{4-5a}=3.3Hz, J_{4-5b}=6.6Hz, H4), 3.796 (1H, dd, J_{4-5a}=3.3Hz, J_{5a-5b}=12.3Hz, H5a), 3.606 (1H, dd, J_{4-5b}=6.6Hz, J_{5a-5b}=12.3Hz, H5b)