

**Prebiotic Carbohydrate Synthesis: Zinc-Proline Catalyzes Direct Aqueous Aldol Reactions
of α -Hydroxy Aldehydes and Ketones**

Jacob Kofoed, Jean-Louis Reymond and Tamis Darbre*

Department of Chemistry and Biochemistry, University of Bern, Freiestrasse 3, CH-3012 Bern, Switzerland.

Fax: +41 31 631 80 57; Tel : +41 31 631 43 70; E-mail: tamis.darbret@ioc.unibe.ch

Supporting Information

NMR and GC spectra.

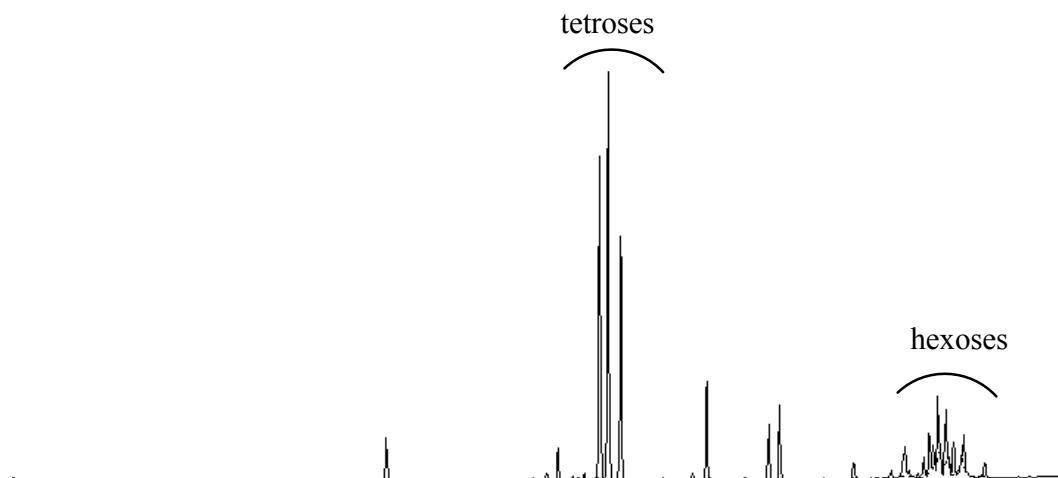


Figure S1. GC of the peracetylated crude from aldolisation of glycolaldehyde.

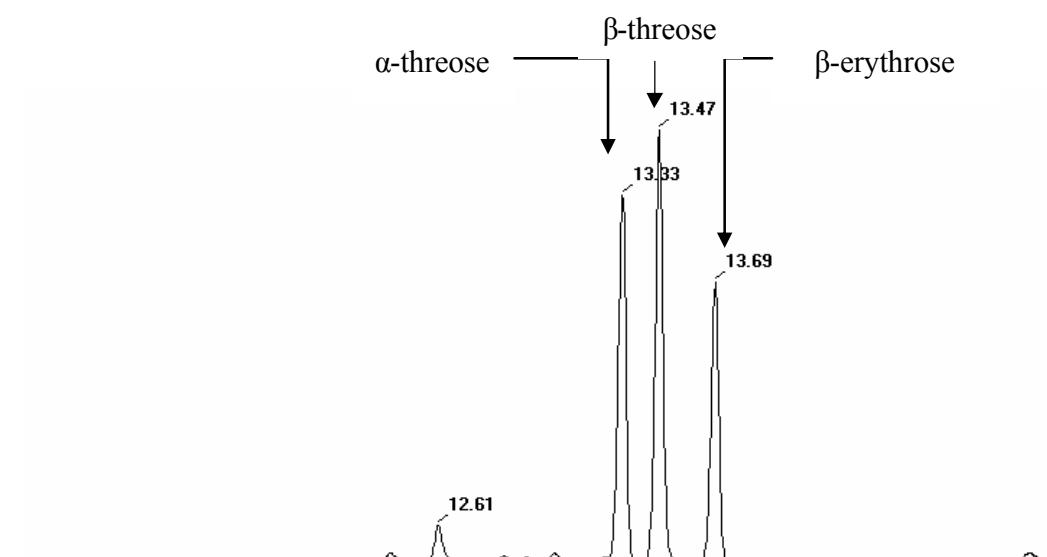


Figure S2. GC of the peracetylated crude sugar mixture showing α -threose, β -threose and β -erythrose (time shown in min).

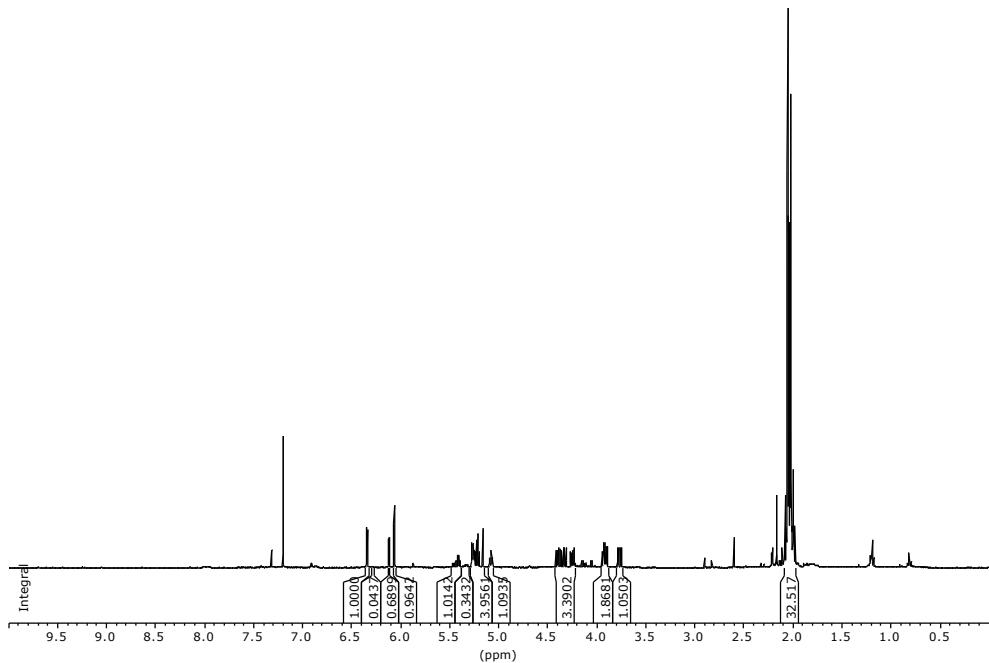


Figure S3. ^1H NMR (500 MHz) in CDCl_3 of the tetrose acetate mixture showing α -threose, β -threose and β -erythrose.

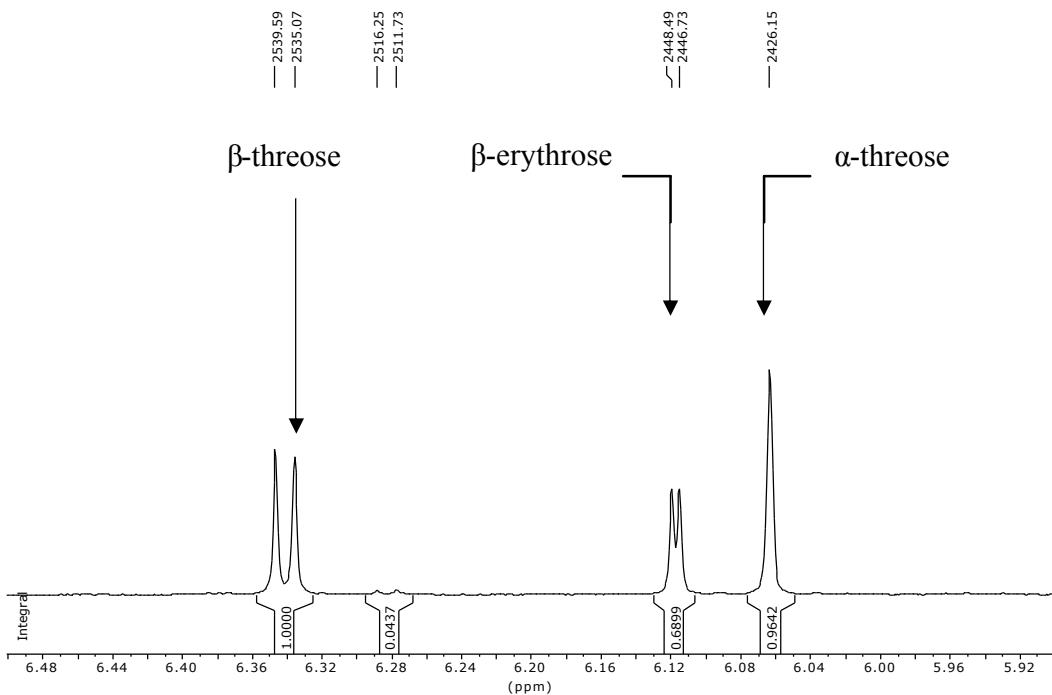


Figure S3. ^1H NMR (CDCl_3 , 500 MHz) showing the anomeric protons of acetylated α -threose, β -threose and β -erythrose.

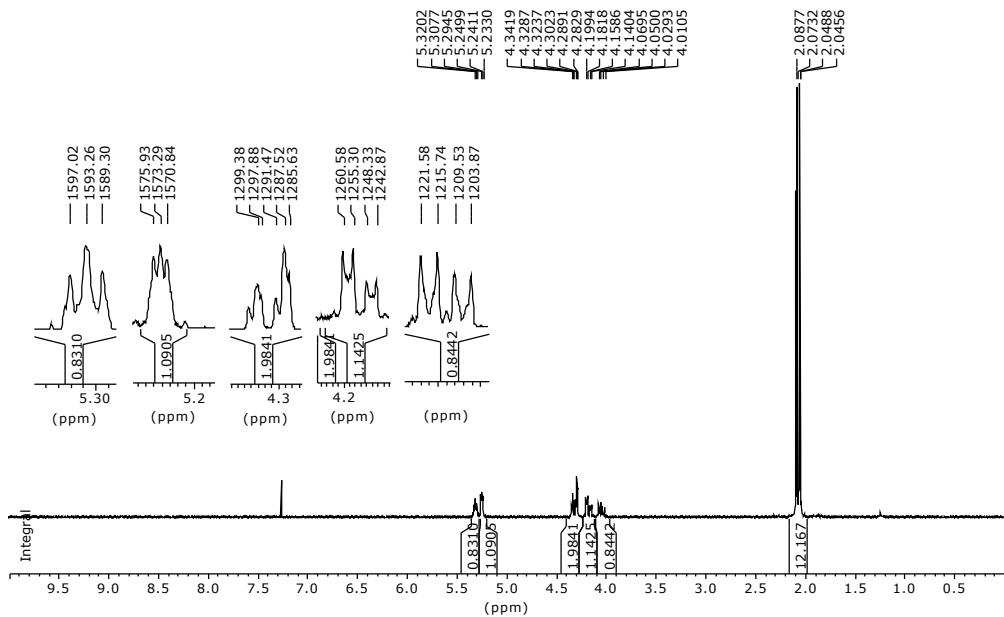


Figure S4. ^1H NMR (CDCl_3 , 300 MHz) of tetrol peracetates.

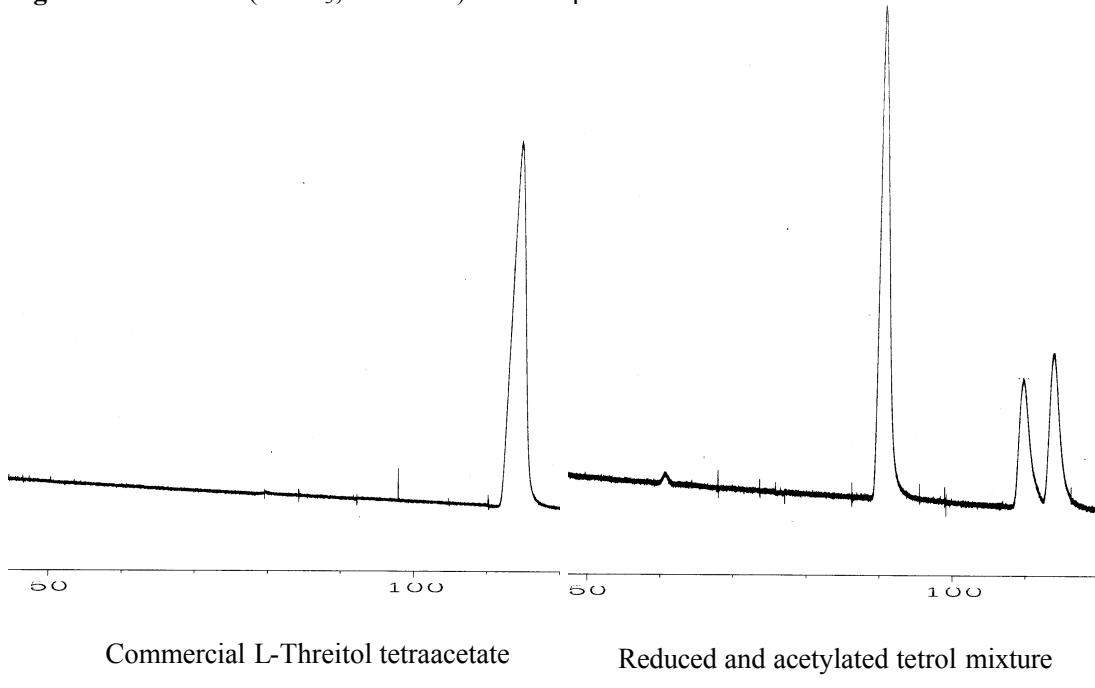


Figure S5. Chiral GC trace of reduced and acetylated tetros showing the *meso*-erythritol and the two enantiomers of threitol.

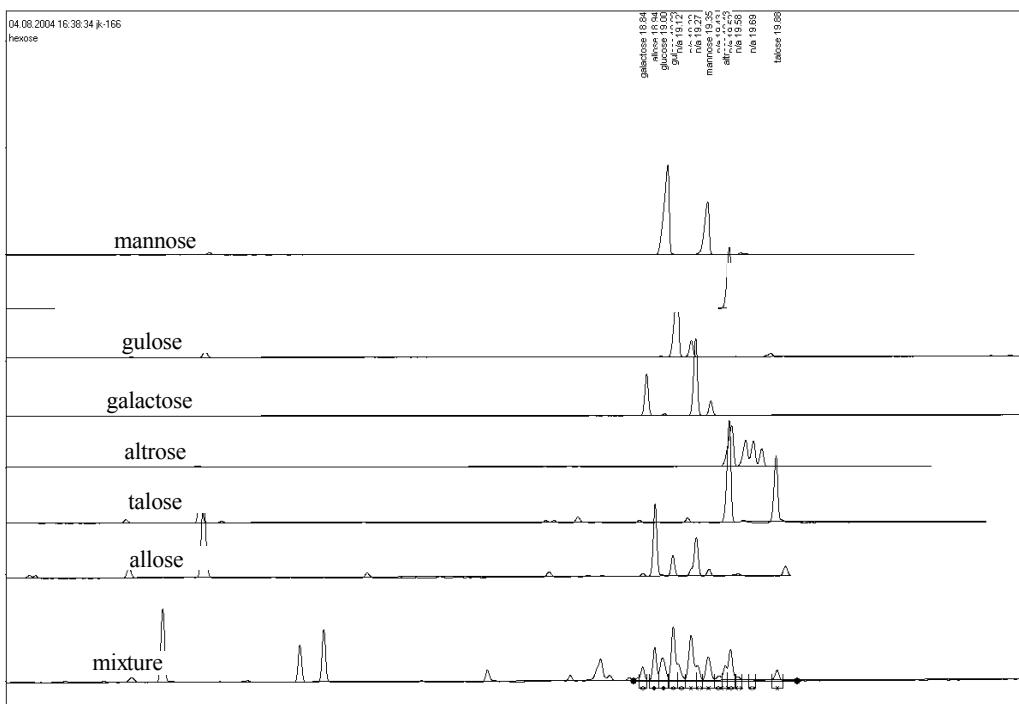


Figure S6. Overlaying of reference sugars and crude mixture from the aldolisation of glycolaldehyde (hexose region).

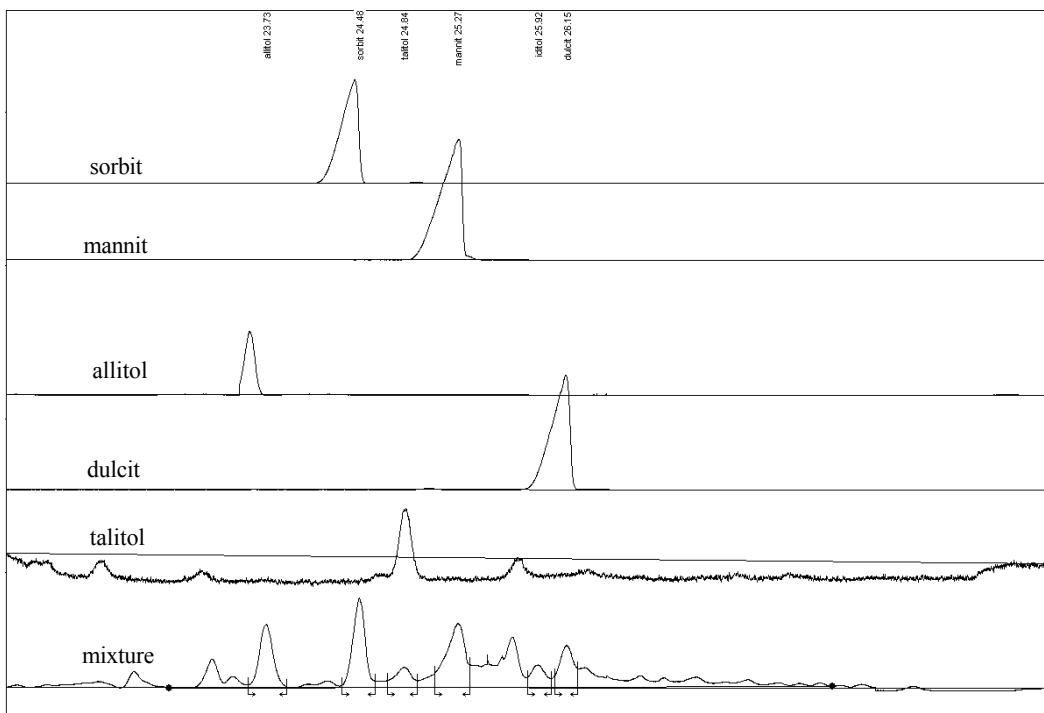


Figure S7. Overlaying of reduced reference sugars and crude mixture from the aldolisation of glycolaldehyde (hexose region).

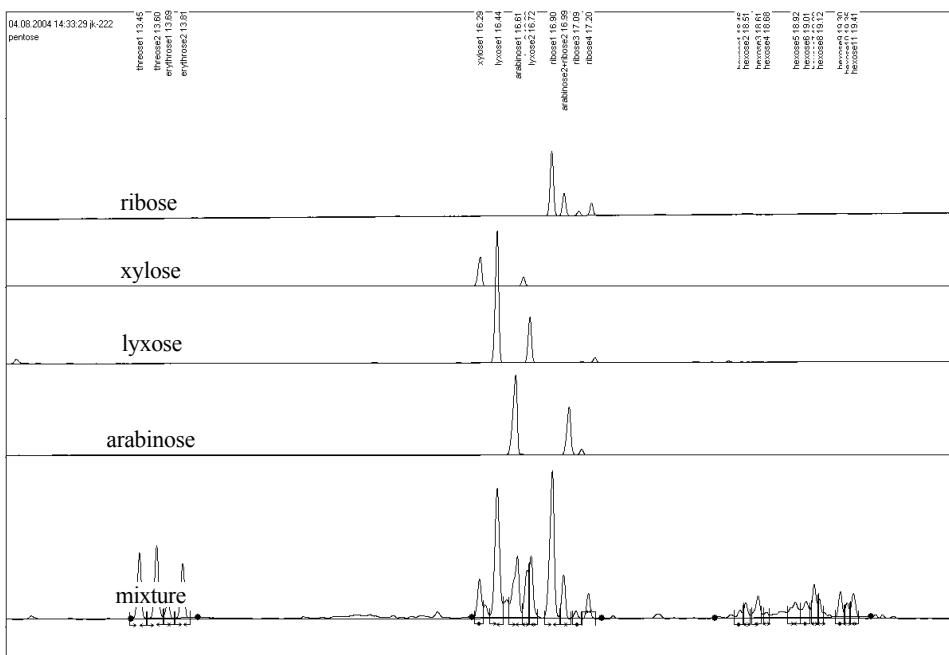


Figure S8. Overlaying of reference sugars and crude mixture from the cross-aldolisation of glycolaldehyde and glyceraldehyde.

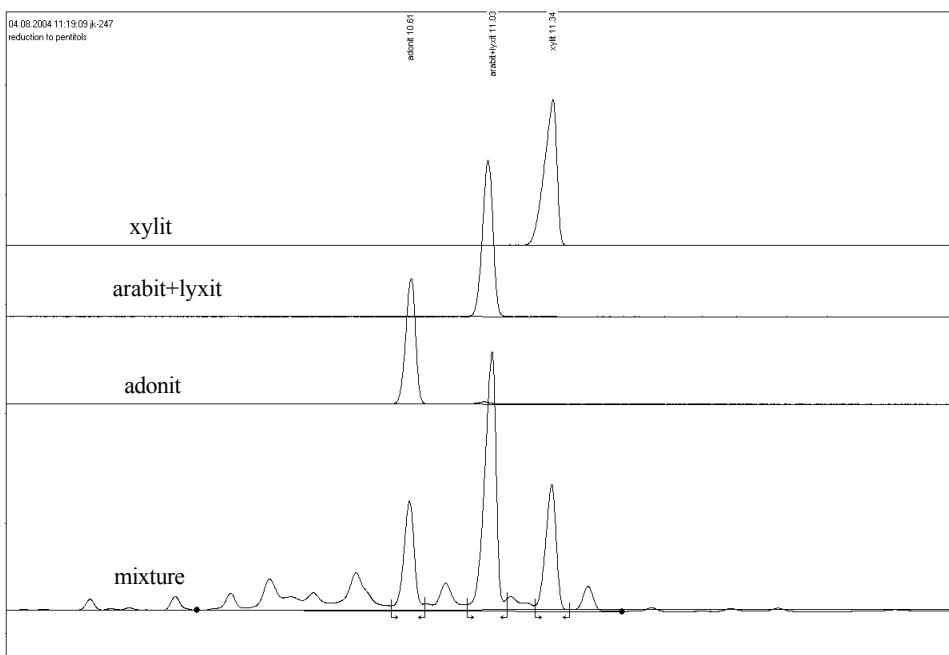


Figure S9. Overlaying of reduced reference sugars and crude mixture from the cross-aldolisation of glycolaldehyde and glyceraldehyde.

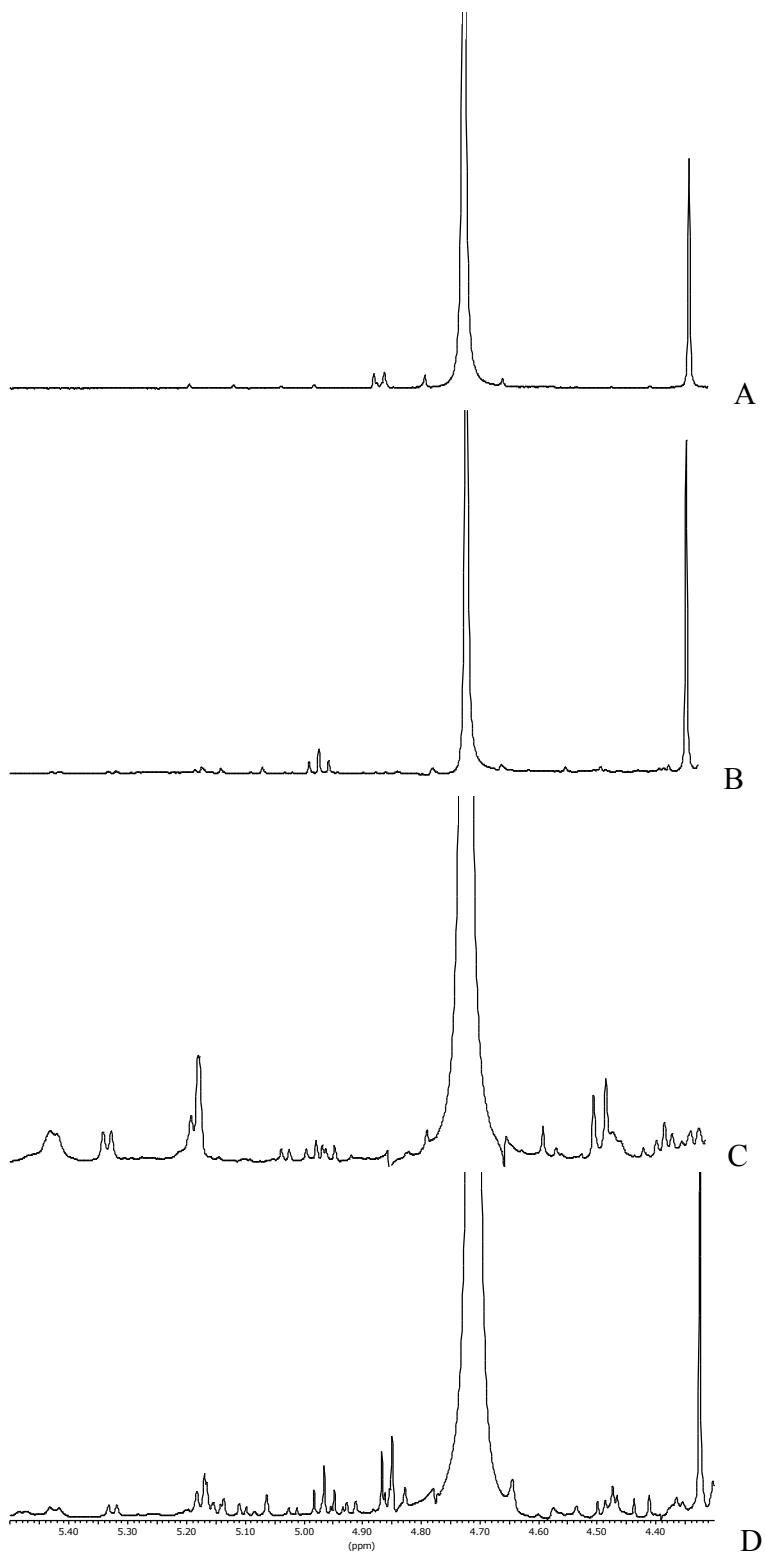


Figure S11. Overlaying of the four different experiments showing the anomeric region. A: ketohexoses, B: ketopentoses, C: tetroses and hexoses, D: tetroses and pentoses.