Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Pathways and their usage in the conversion of carbohydrates by aqueous barium hydroxide: insights from hyperpolarized and quantitative NMR

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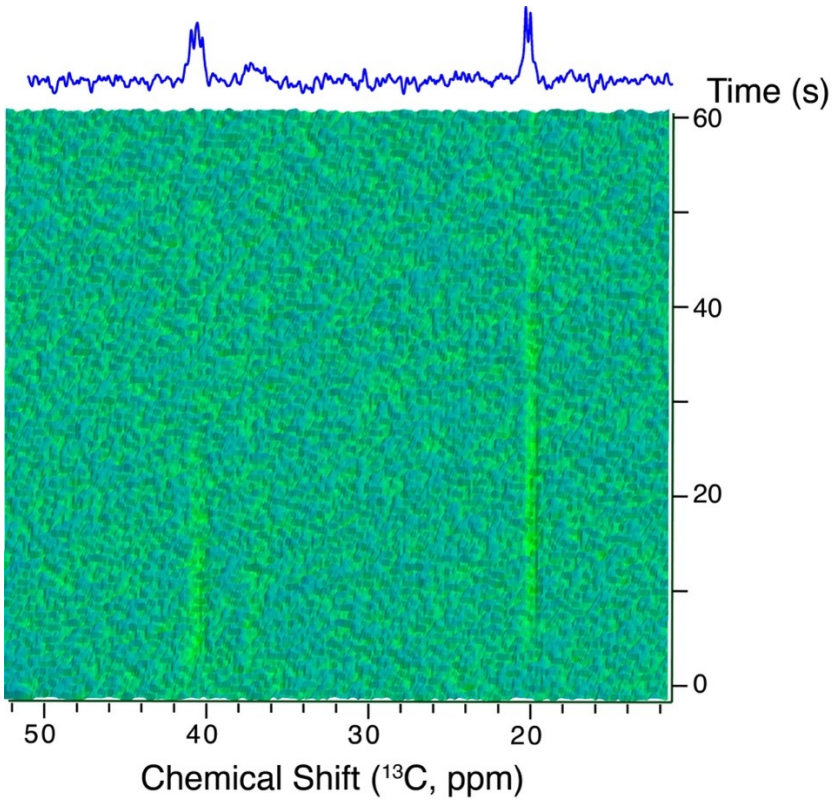

Fig. S1. D-DNP experiment showing the conversion of hyperpolarized [U-^{2}H, ^{13}C] glucose in the presence of barium hydroxide. A time series of ^{13}C NMR spectra was acquired by exciting a ^{13}C NMR spectrum using a 10° flip angle pulse each second. The sum spectrum for the first 60 spectra acquired after glucose injection into 250 mM $Ba(OH)_2$ at 60 °C is shown on top, clarifying the presence of signal near 40.5 ppm (tentatively assigned to C3 of 3-deoxyglucosone), a broader population near 37 ppm (tentatively assigned to metasaccharinic acid C3) and 20 ppm (lactate C3). Reaction conditions: 250 mM $Ba(OH)_2$, 6 mM hyperpolarized [U-^{13}C, U-^{2}H] glucose, 60 °C, D_2O.

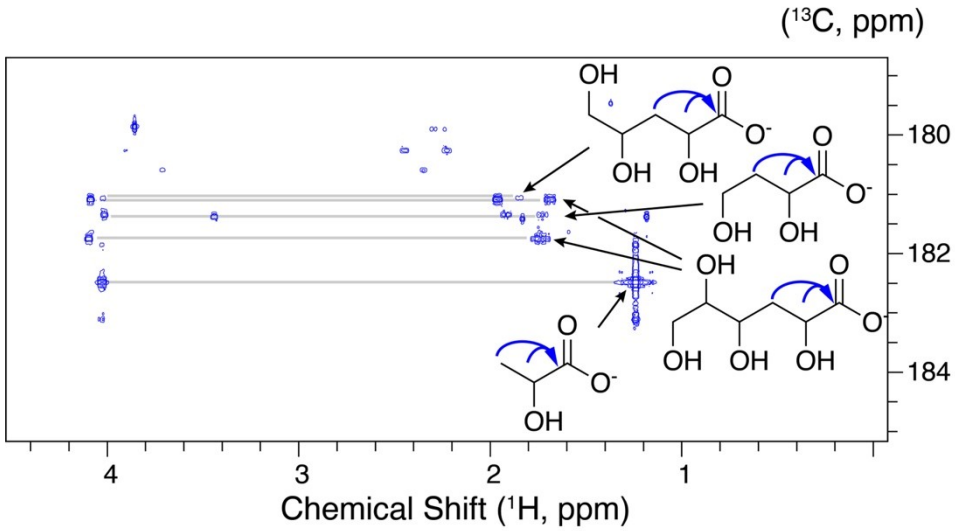

Fig. S2. Selective ^{1}H-^{13}C HMBC acquired on post-reaction material of glucose conversion by barium hydroxide. Correlations of alcoholic CH signals at C2 and aliphatic groups at C3 to the carboxylic acid groups in lactate and in analogous metasaccharinic acids of length C4-C6 are shown. Reaction conditions: 250 mM $Ba(OH)_2$, 100 mM glucose, 30 ºC, nitrogen atmosphere, H_2O solvent, 24 hours.

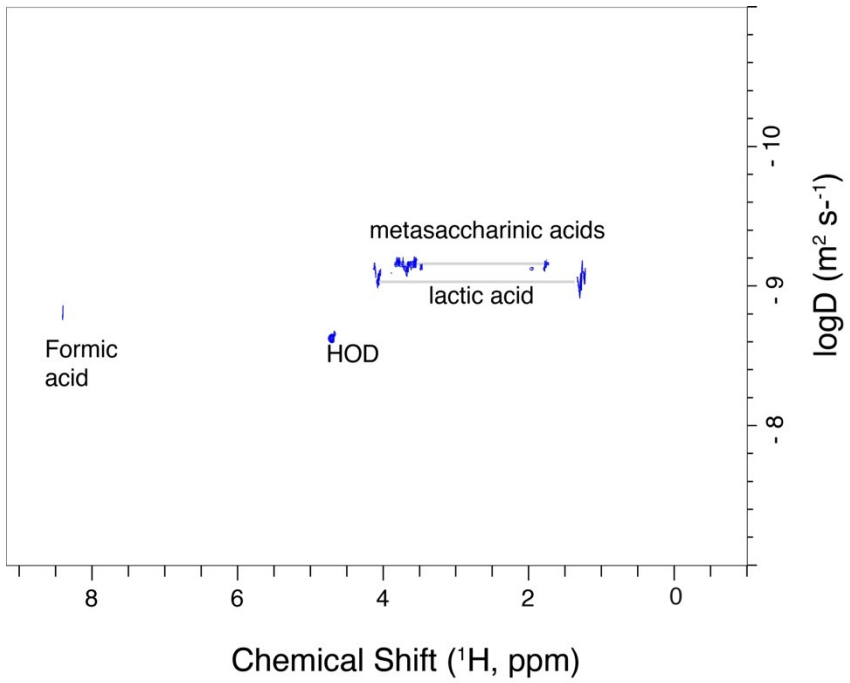

Fig. S3. ^{1}H diffusion ordered spectroscopy (DOSY NMR) on the product mixture after conversion of glucose in aqueous barium hydroxide, showing the presence of minor formic acid in addition to lactic acid and larger metasaccharinic acid signals, where the latter show signals of alcohol and methylene groups. Reaction conditions: 250 mM $Ba(OH)_2$, 100 mM glucose, 30 ºC, nitrogen atmosphere, D_2O solvent, 24 hours.

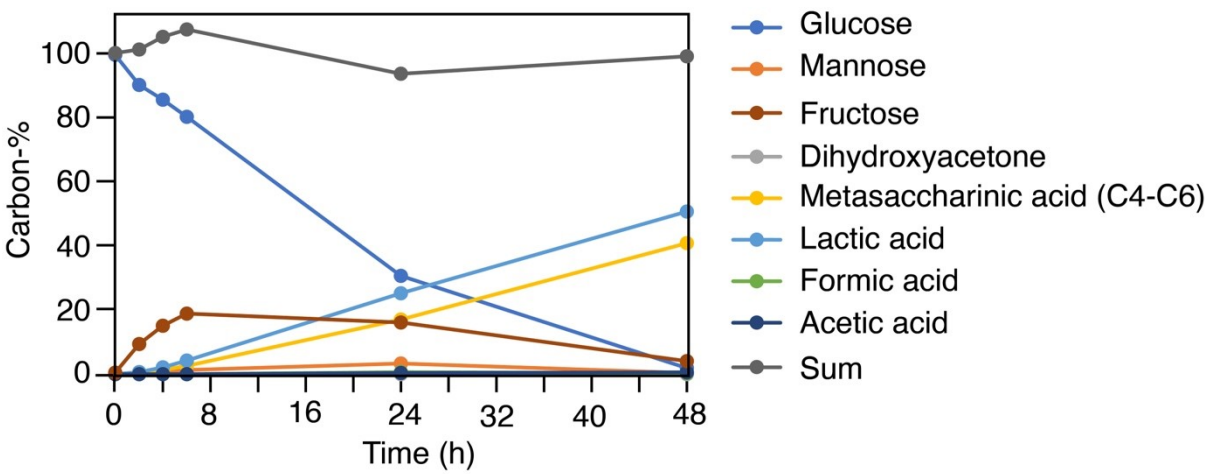

Fig. S4. Time course of quantified chemicals in the conversion of glucose by aqueous barium hydroxide. Reaction conditions: 250 mM $Ba(OH)_2$, 100 mM glucose, 20 ºC, nitrogen atmosphere, H_2O solvent, variable time.

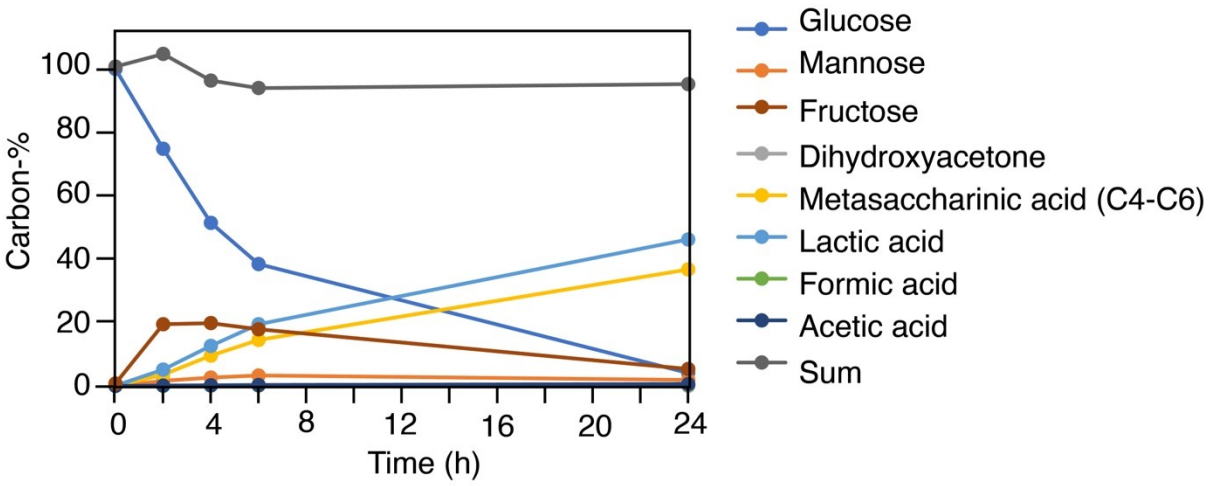

Fig. S5. Time course of quantified chemicals in the conversion of glucose by aqueous barium hydroxide. Reaction conditions: 250 mM $Ba(OH)_2$, 100 mM glucose, 30 ºC, nitrogen atmosphere, H_2O solvent, variable time.

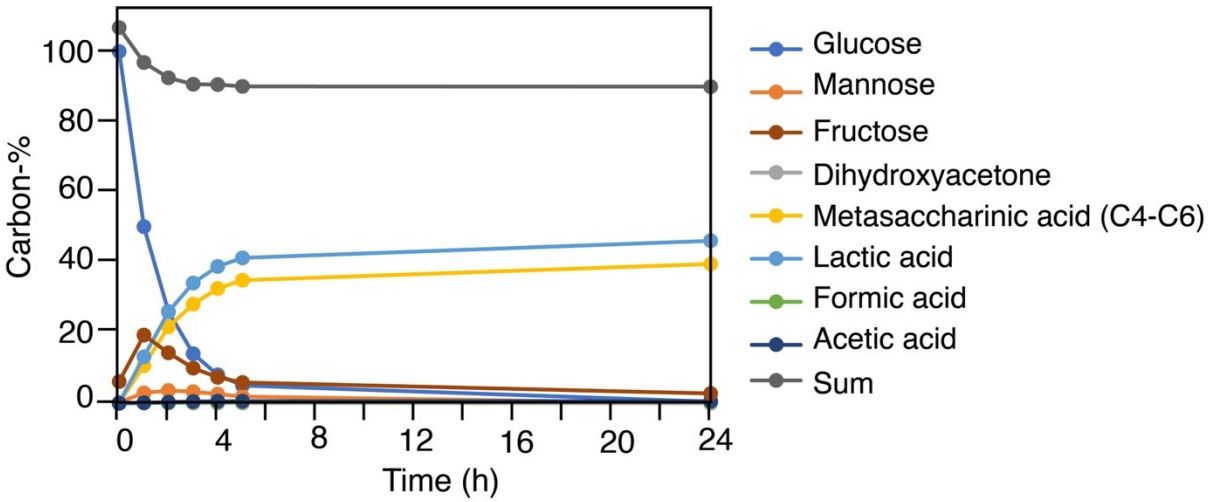

Fig. S6. Time course of quantified chemicals in the conversion of glucose by aqueous barium hydroxide. Reaction conditions: 250 mM $Ba(OH)_2$, 100 mM glucose, 40 ºC, nitrogen atmosphere, H_2O solvent, variable time.

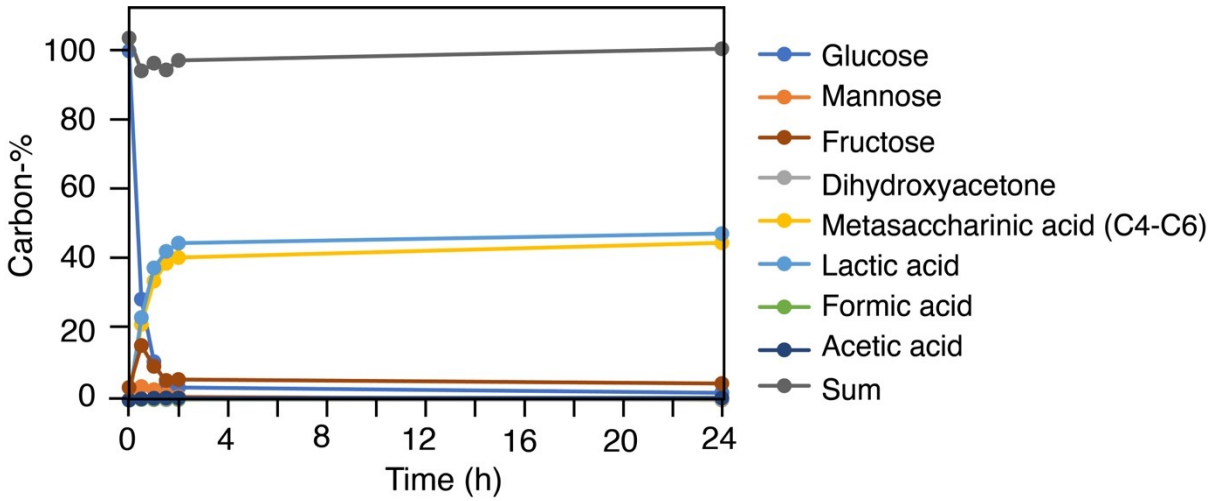

Fig. S7. Time course of quantified chemicals in the conversion of glucose by aqueous barium hydroxide. Reaction conditions: 250 mM $Ba(OH)_2$, 100 mM glucose, 50 ºC, nitrogen atmosphere, H_2O solvent, variable time.

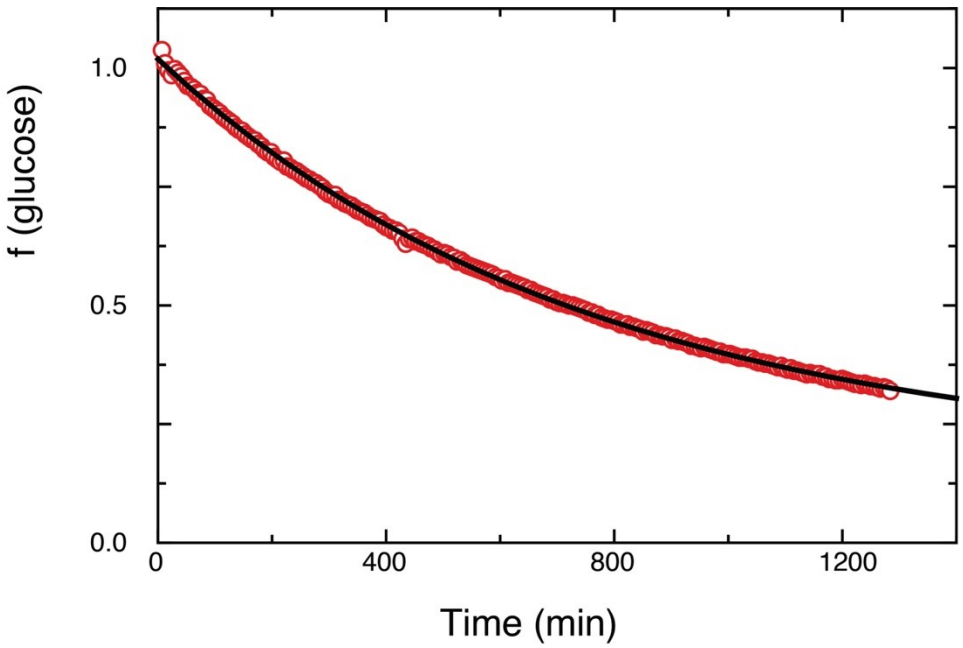

Fig. S8. Time course for substrate signal area (anomeric $Glc^{\alpha-pyr}$ signal) in the ^{1}H - NMR detected conversion of glucose by aqueous barium hydroxide. Data were acquired on an 800 MHz instrument equipped with a TCI cryoprobe with a time resolution between individual ^{1}H NMR spectra of 3.1 minutes. Reaction conditions: 250 mM $Ba(OH)_2$, 100 mM glucose, 30 °C, 90% H_2O/10% D_2O solvent (500 μl).

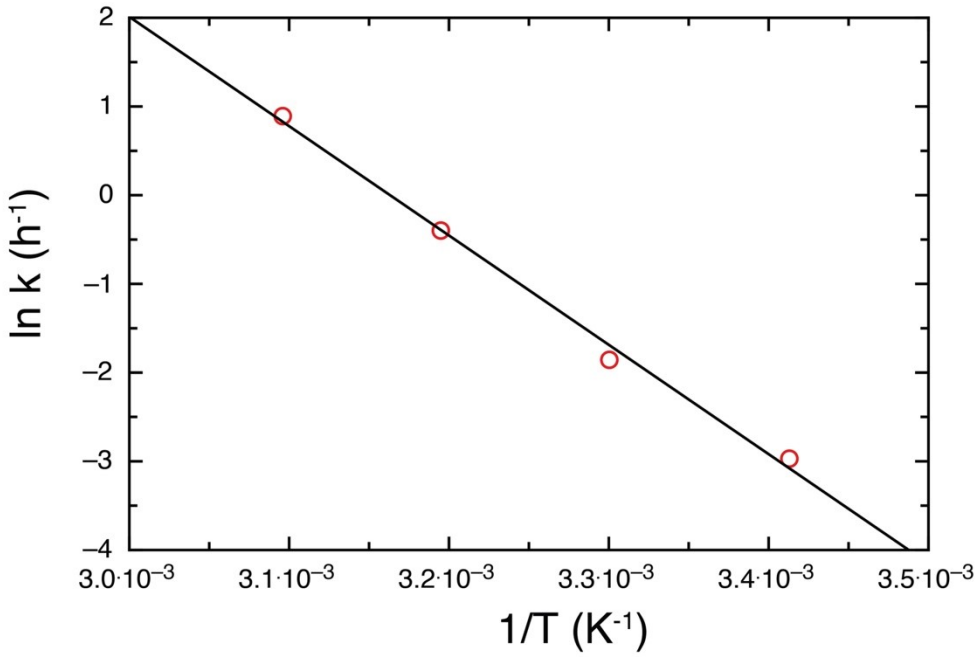

Fig. S9. Arrhenius plot for the conversion of glucose in aqueous barium hydroxide at 293 K, 303 K, 313 K and 323 K as shown in Figs. S10-S13. Reaction rate constants derive from a first order kinetics (exponential fit) of the substrate signal. Arrhenius analysis yields an energy of activation of 102 ±5 kJ/mol.

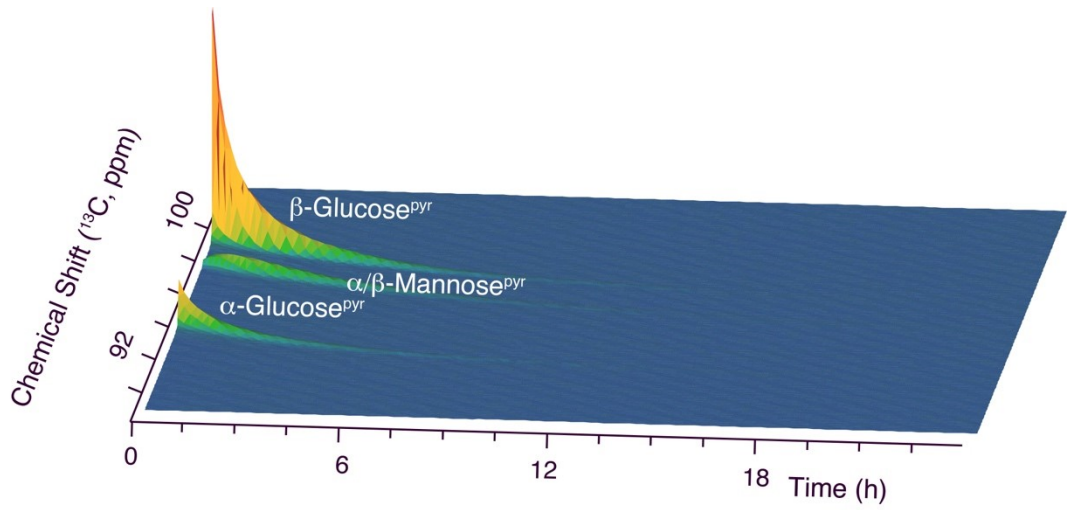

Fig. S10. Time course for carbohydrate anomeric signals in the ^{13}C -NMR detected conversion of [1-^{13}C] glucose by aqueous barium hydroxide. Data were acquired on an 800 MHz instrument equipped with a TCI cryoprobe with a time resolution between individual ^{13}C NMR spectra of 12.5 minutes. Reaction conditions: 250 mM $Ba(OH)_2$, 100 mM [1-^{13}C] glucose, 40 °C, 90% H_2O/10% D_2O solvent (500 μl).

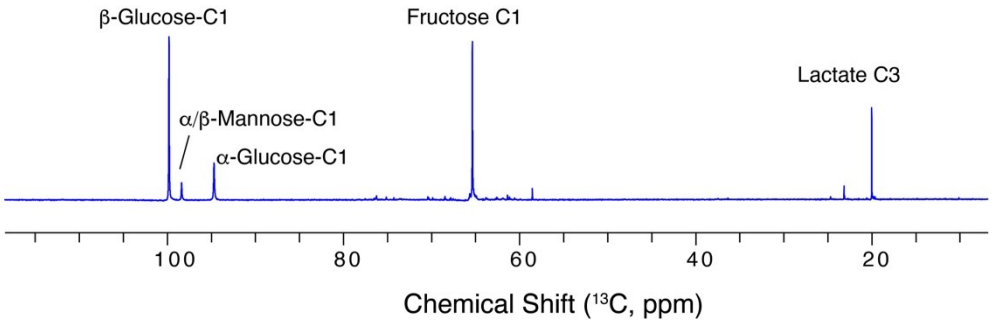

Fig. S11. Individual ^{13}C NMR spectrum from the time series shown in Fig. S1 with chemicals and ^{13}C positions assigned to the most prominent NMR signals.

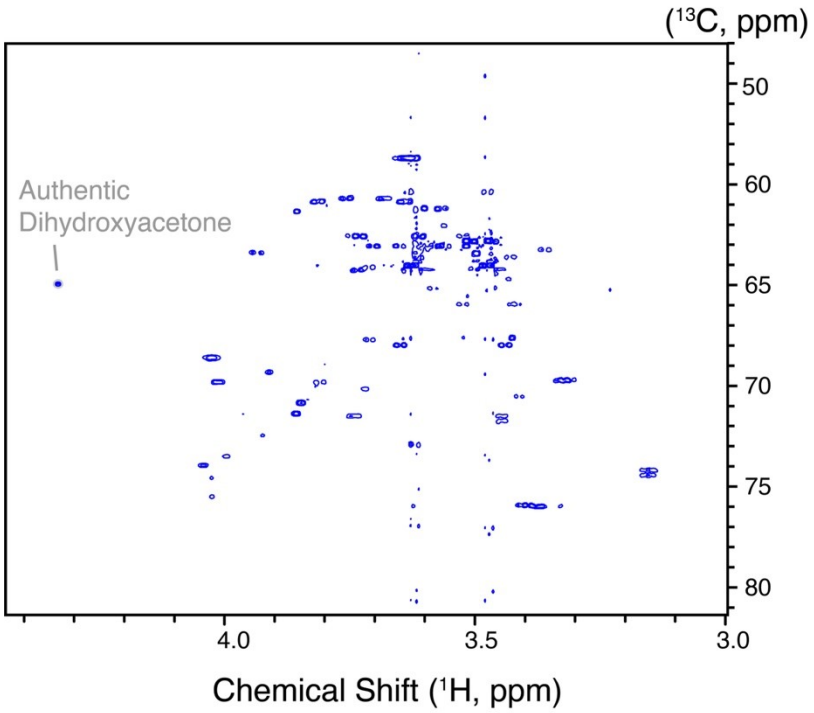

Fig. S12. ^{1}H-^{13}C HSQC spectrum for the identification of the characteristic dihydroxyacetone CH signal by comparison of the reaction mixture (blue) and authentic reference standard (grey). Reaction conditions: 250 mM $Ba(OH)_2$, 20 mM [1-^{13}C] glucose, 30 ºC, nitrogen atmosphere, H_2O solvent, 4 hours reaction time.

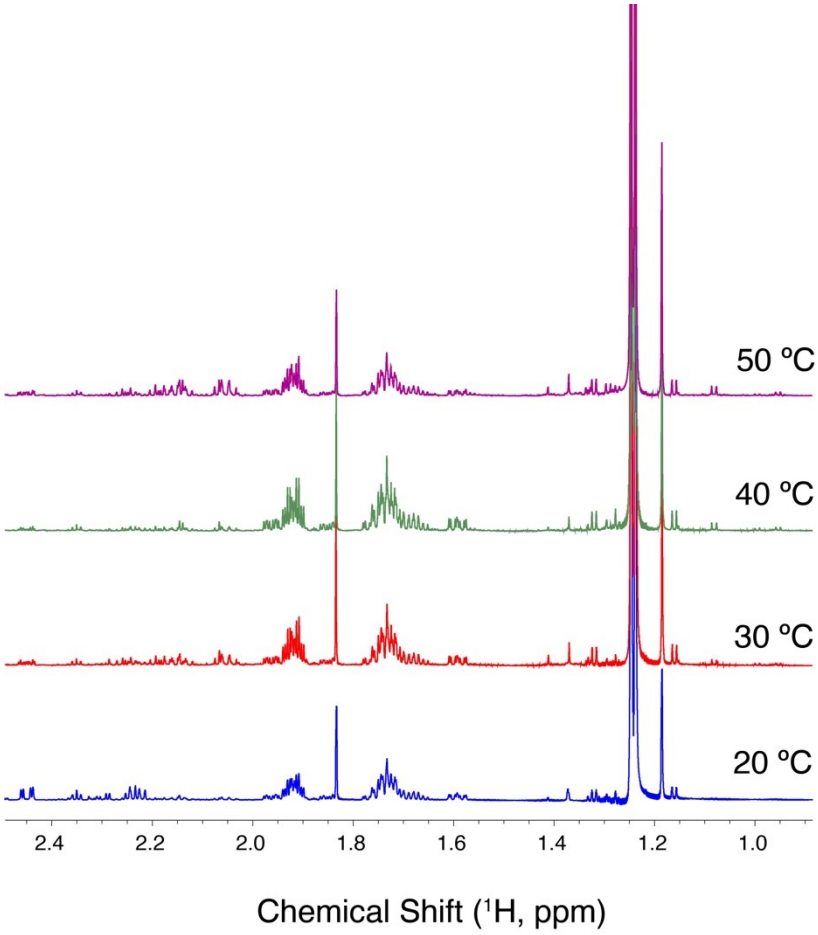

Fig. S13. ^{1}H NMR spectra (800 MHz) acquired after the conversion of 100 mM glucose at variable temperatures by barium hydroxide. Spectra indicate that metasaccharinic acid formation (multiplets between 1.6 and 2.0 ppm) does not systematically depend on the substrate concentration. Reaction conditions: 250 mM $Ba(OH)_2$, 100 mM glucose, variable temperature as indicated, nitrogen atmosphere, H_2O, after 24 hours (30, 40, 50 ºC) and after 48 hours for the reaction at 20 ºC.

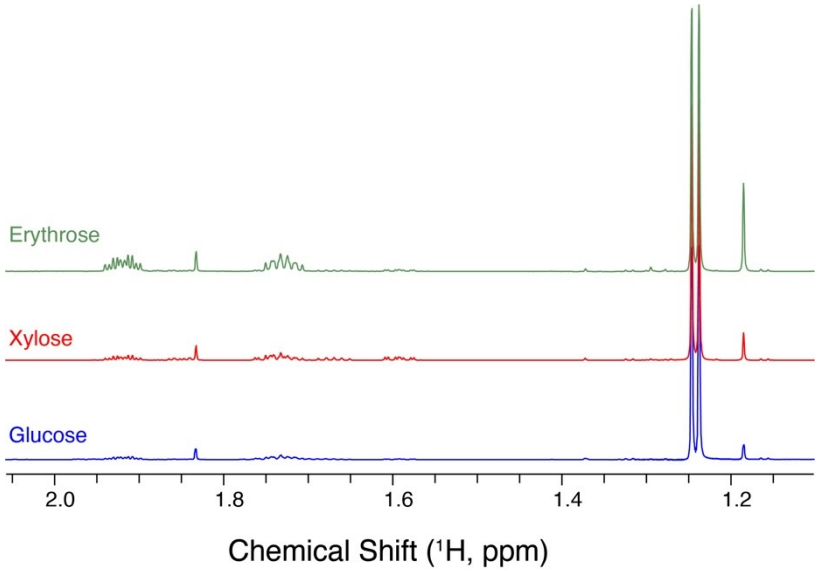

Fig. S14. ^{1}H NMR spectra (800 MHz) acquired after the conversion of 100 mM glucose or xylose and 25 mM erythrose by queous barium hydroxide. Spectra indicate that metasaccharinic acid formation (multiplets between 1.6 and 2.0 ppm) increase at shorter substrate length relative to lactate (doublet at 1.25 ppm). Reaction conditions: 250 mM $Ba(OH)_2$, 100 mM glucose, variable temperature as indicated, nitrogen atmosphere, H_2O, after 24 hours (30 ºC, 40 ºC, and 50 ºC) and after 48 hours for the reaction at 20 ºC.

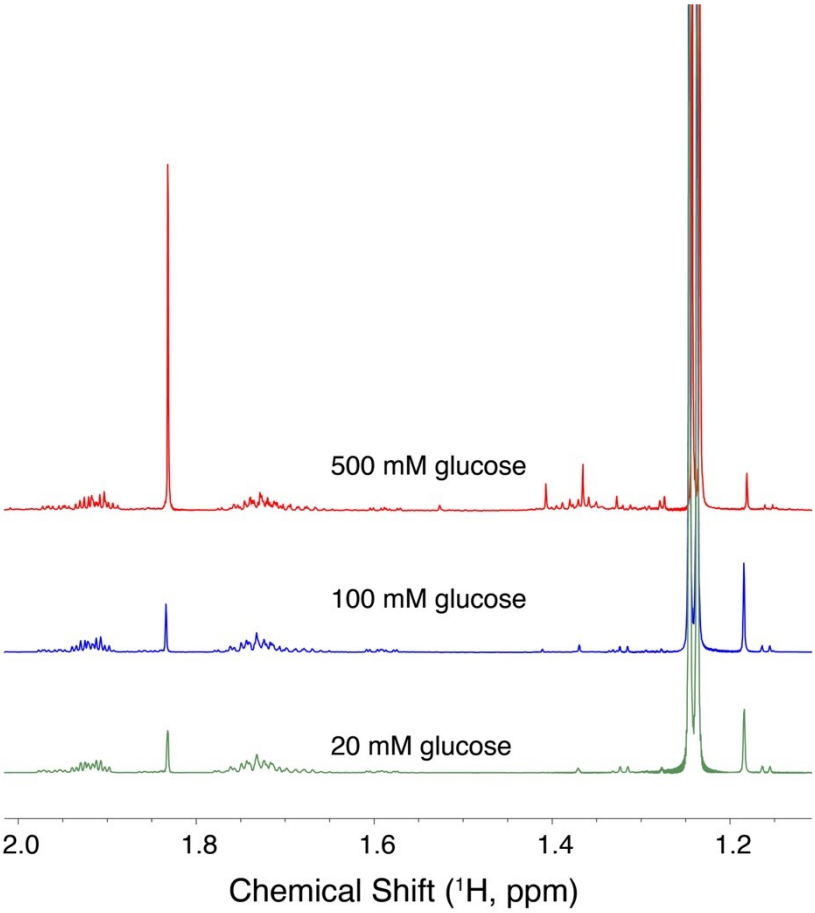

Fig. S15. ^{1}H NMR spectra (800 MHz) acquired after the conversion of various glucose concentrations as indicated by barium hydroxide. Spectra are normalized to identical lactate signal areas (doublet at 1.25 ppm) and indicate that metasaccharinic acid formation (multiplets between 1.6 and 2.0 ppm) does not strongly depend on the substrate concentration. Reaction conditions: 250 mM $Ba(OH)_2$, variable glucose concentrations as indicated, nitrogen atmosphere, 30 ºC temperature, H_2O solvent, 24 hours.

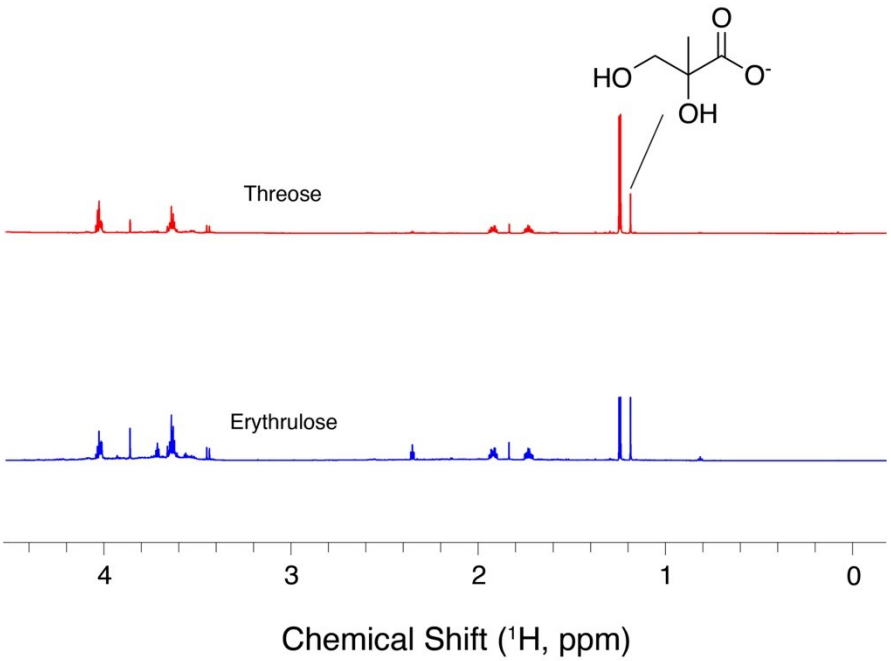

Fig. S16. ^{1}H -NMR spectrum acquired after the conversion of C4 carbohydrates by barium hydroxide, showing the high fraction of metasaccharinic acid (multiplets at 1.6-2 ppm) and branched byproduct, especially from intrinsically acyclic erythrulose substrate. Reaction conditions: 250 mM $Ba(OH)_2$, 100 mM erythrulose or 25 mM threose, 30 ºC, nitrogen atmosphere, H_2O solvent, 24 hours.

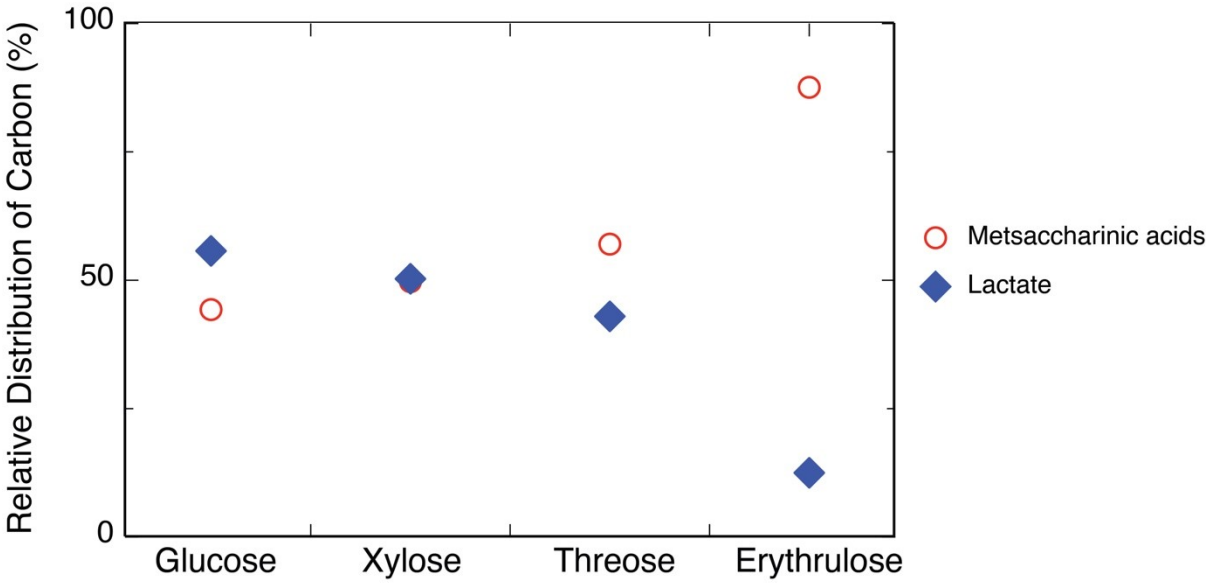

Fig. S17. Relative distributions between lactate and longer 3-deoxy acid products by barium hydroxide, showing increasing competition of metasaccharinic acid formation with lactate formation for higher acyclic substrate fraction (the fraction of acyclic species increases from left to right).

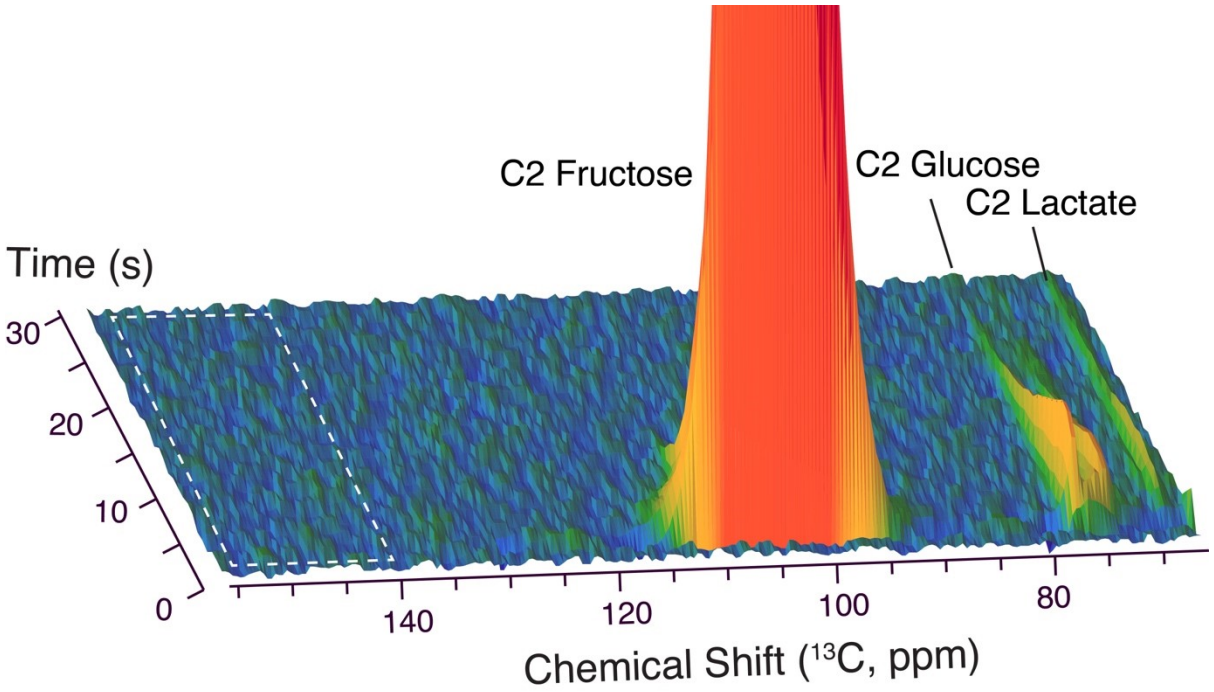

Fig. S18. D-DNP experiment showing the conversion of hyperpolarized [2-^{13}C] fructose in the presence of sodium hydroxide in analogy to the experiment with barium hydroxide (Figure 1 in the manuscript). A time series of ^{13}C NMR spectra was acquired using a 10° flip angle pulse. Signals from the C2 position of glucose and lactate emerge, while enol species in the ^{13}C chemical shift range 140-155 ppm are not detectable, thus indicating a role of divalent cations in the stabilization of the enol species. Reaction conditions: 500 mM NaOH, 6 mM hyperpolarized [2-^{13}C] fructose, 60 °C, D_2O solvent.