Supplementary information for

Sn-Beta Catalysed Conversion of Hemicellulosic Sugars

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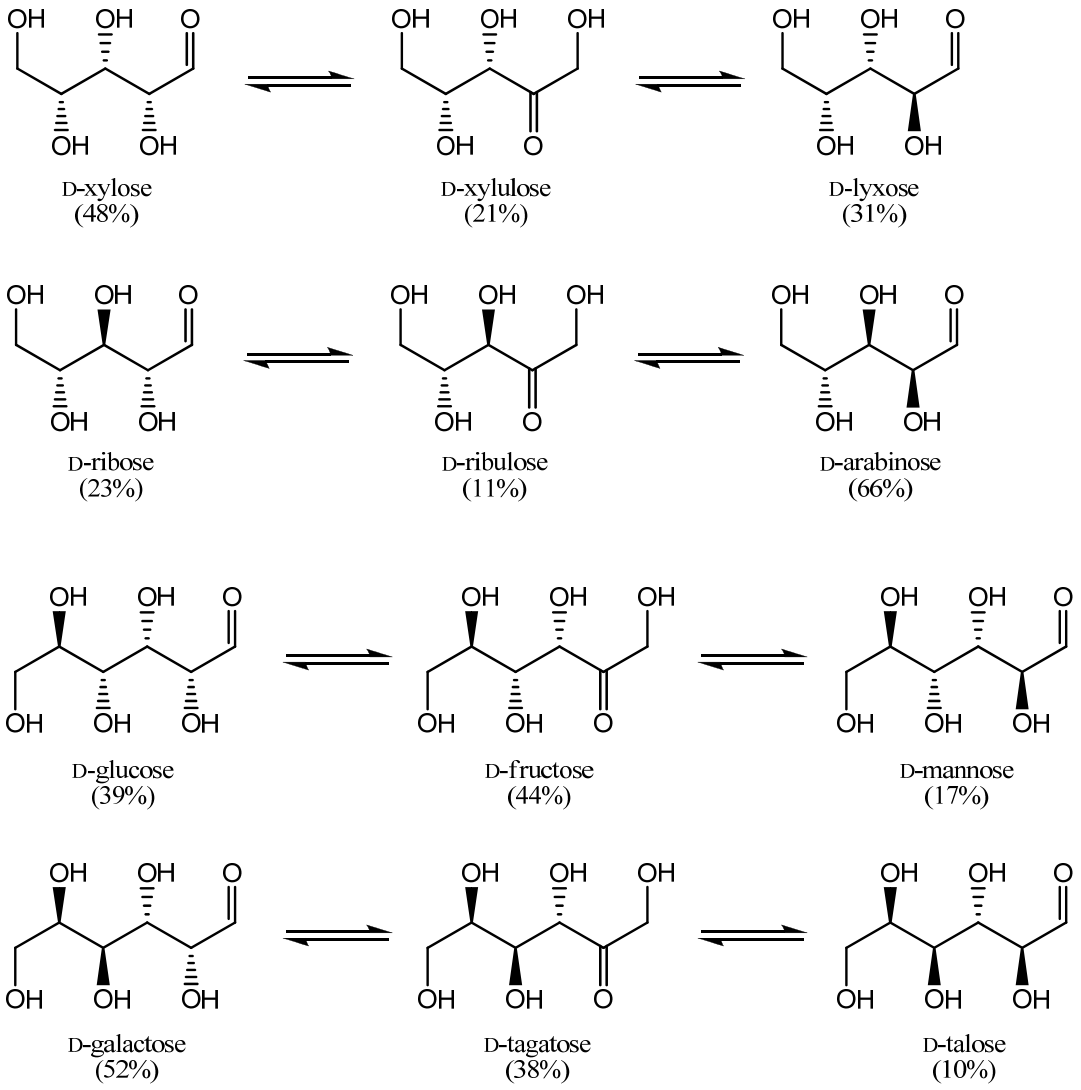
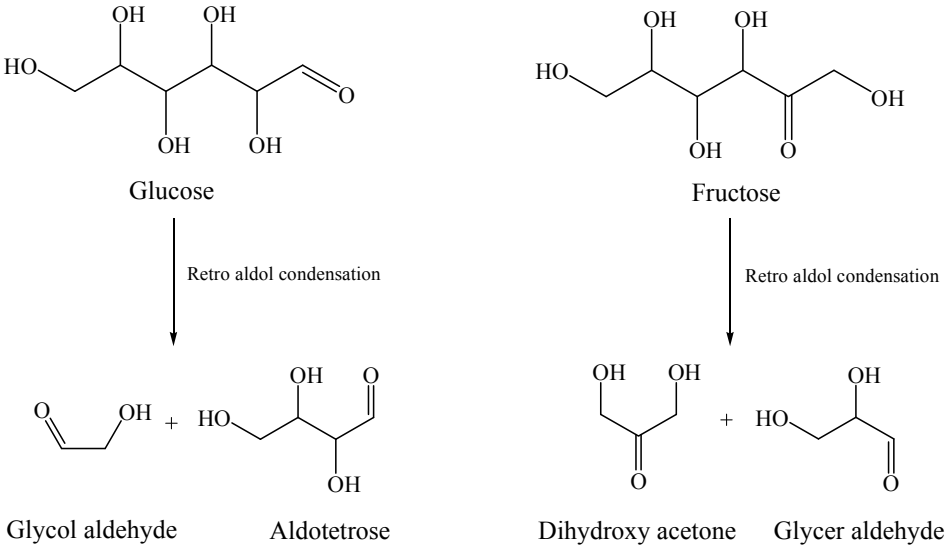
HPLC analysis procedure for sugar isomerisation experiments

Samples taken after reaction were analyzed by HPLC. By-product concentrations of glycoaldehyde and lactic acid were determined in an HPLC Waters e2695 system with an Aminex HPX-87H (Biorad) column, using MiliQ water (pH=2) as mobile phase at a rate of 0.6 ml min^{-1}, and column temperature of 80 °C. Hexoses, pentoses, 5-hydroxymethylfurfural (HMF), and furfural concentrations were analyzed in a Waters HPLC e2695 system containing an Aminex HPX-87P (Biorad) column, using MiliQ water (pH=7) as mobile phase at a rate of 0.6 ml min^{-1}, and column temperature of 85 °C. Both HPLC instruments are equipped with Waters 2414 refractive index (RI) detectors and Waters 2998 PDA UV detectors.

It should be noted that for a typical analysis of a xylose or lyxose isomerized solution in the Aminex HPX-87P column (Biorad) a series of peaks were identified corresponding to xylose, lyxose, xylulose and furfural. By injecting standards of xylose, lyxose, and xylulose we determined that lyxose and xylulose peaks eluted at very similar retention times. When analyzing xylose and xylulose in the PDA UV detector the response factor for xylulose is higher by a factor of 26 relative to lyxose at a wavelength of 210 nm, while the response factors of these two pentoses in the RI detector are similar. Therefore, the concentrations of xylulose and lyxose were determined from solving a linear combination of the peak areas present in both the PDA UV signal at 210 nm and the RI signal.[1]



Scheme S1. Isomerisation of the four monosaccharide families: xylose-xylulose-lyxose, ribose-ribulose-arabinose, glucose-fructose-mannose and galactose-tagatose-talose. The numbers in parenthesis are the equilibrium values obtained at 100 °C in water from this study using Sn-Beta as the isomerisation catalyst.



Scheme S2. Retro-aldol condensation of glucose and fructose.

Table S1. Carbon balance for the sugar isomerisation experiments in Figure 1.[a]								
	0 min	15 min	30 min	1 hour	2 hours	4 hours	20 hours	43 hours
Glucose	-	100 (100)	103 (103)	102 (102)	94 (94)	89 (88)	73 (66)	70 (58)
Fructose	-	100 (100)	100 (100)	95 (95)	88 (88)	86 (82)	72 (61)	72 (59)
Mannose	-	102 (102)	101 (101)	99 (99)	92 (92)	87 (85)	74 (67)	71 (59)
Galactose	-	100 (100)	95 (95)	90 (89)	90 (89)	77 (75)	64 (51)	57 (41)
Xylose	-	101 (101)	100 (96)	95 (84)	90 (75)	89 (68)	83 (41)	85 (39)
Lyxose	-	100 (100)	100 (96)	95 (88)	96 (81)	85 (66)	83 (40)	88 (39)
Arabinose	-	100 (100)	97 (94)	91 (85)	86 (76)	83 (61)	82 (35)	83 (34)
Ribose	-	91 (91)	87 (83)	85 (77)	80 (67)	80 (55)	76 (32)	81 (30)

[a] The carbon balance is defined as the: (sum of the moles of carbon in the product)/(moles of carbon in the substrate). The number in parenthesis is defined as the (sum of the moles of the 3 sugars)/(moles of the sugar in the feed from start) as determined by HPLC analysis. This constitutes primarily sugars, lactic acid, HMF, furfural and glycoaldehyde.

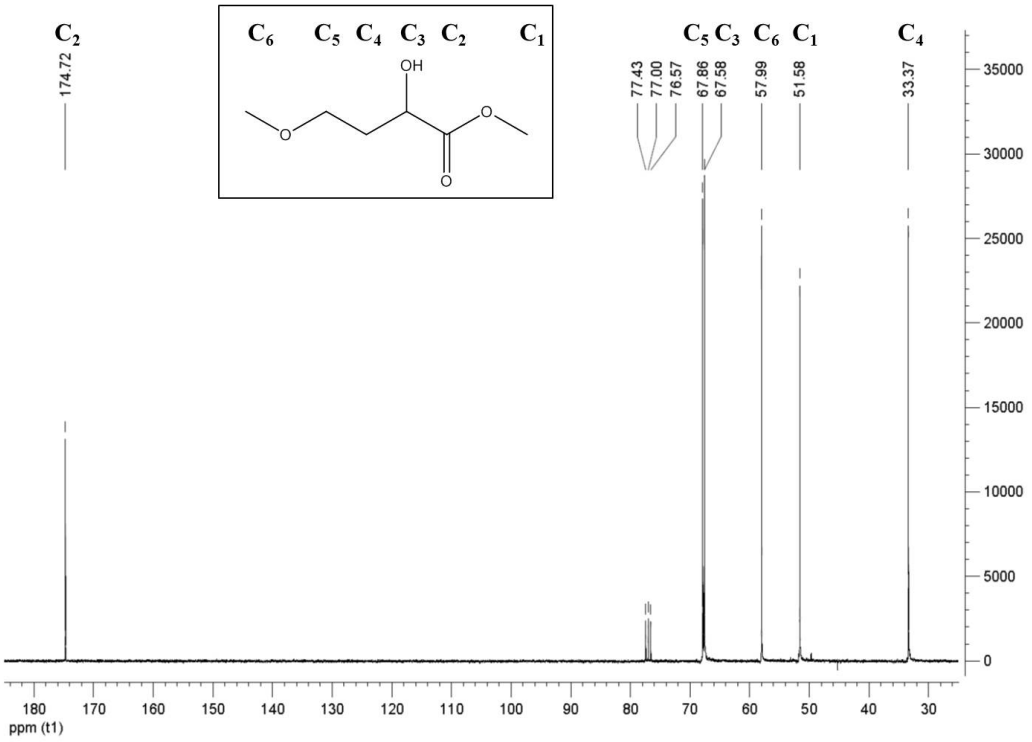


Figure S1. ^{13}C NMR carbon spectrum of methyl 2-hydroxy-4-methoxybutanoate recorded in $CDCl_3$ (recorded at 75.5 MHz). MMHB was isolated from the reaction mixture by column chromatography using an ethyl acetate and dichloromethane mixture (15:85).

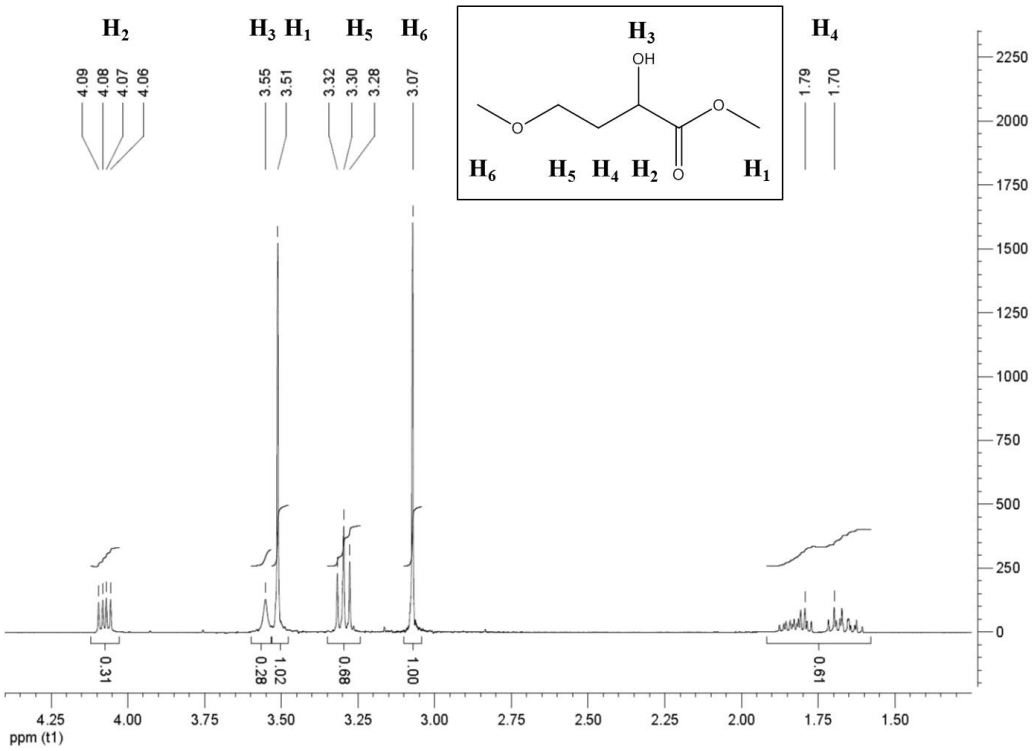


Figure S2. ^{1}H NMR proton spectrum of methyl 2-hydroxy-4-methoxybutanoate isolated from the reaction mixture recorded in $CDCl_3$. Instrument used was a Varian Mercury 300 MHz NMR.

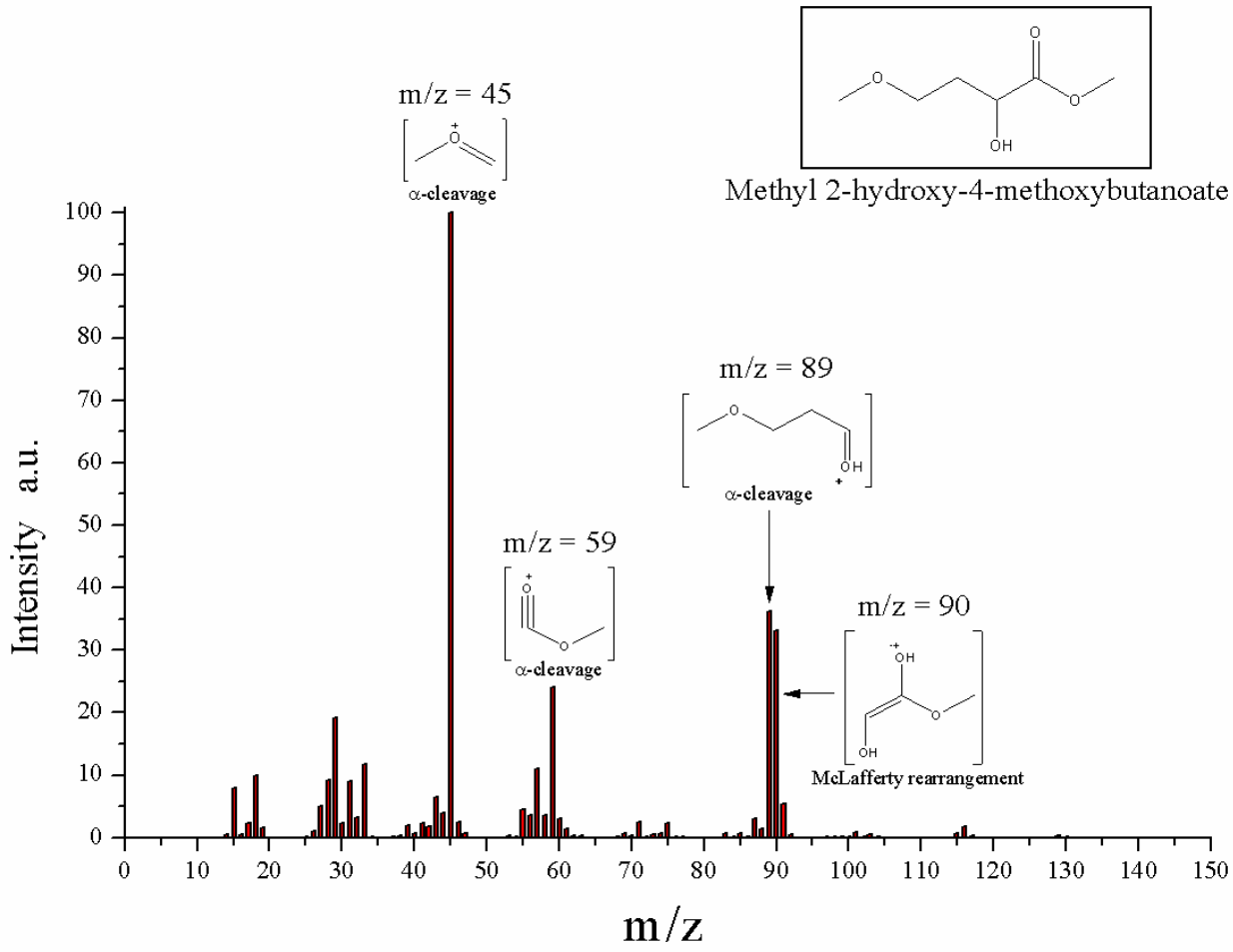


Figure S3. Fragmentation pattern of methyl 2-hydroxy-4-methoxybutanoate isolated from the reaction mixture from GC-MS using electron ionisation.

FT-IR characterization using d3-acetonitrile as a probe molecule

A self-supporting wafer of the Sn-beta catalyst was pressed and degassed at 350 °C for 4 hours. Transmission spectra of stepwise desorption of d3-acetonitrile from the saturated sample is shown in Figure S4. The bands located at 2276 cm^{-1} and 2267 cm^{-1} are designated to acetonitrile coordinated to silanols and physisorbed acetonitrile, respectively. The strongly red-shifted bands at 2317 cm^{-1} and 2307 cm^{-1} arise from acetonitrile coordinated to strong Lewis acidic tin sites. The band shifted to 2317 cm^{-1} has previously been designated to tin sites having one bond hydrolyzed whereas the 2307 cm^{-1} band represents tetrahedrally incorporated tin. [2,3]

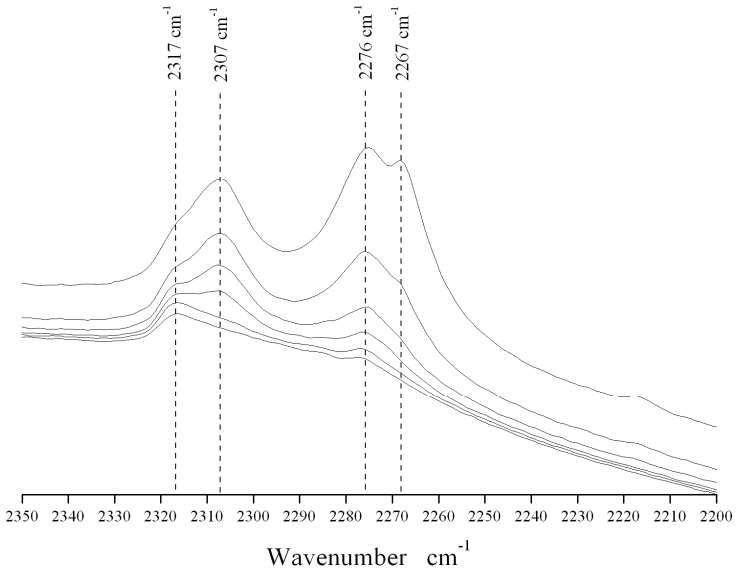


Fig. S4. FT-IR spectra of stepwise desorption of d3-acetonitrile from a degassed Sn-Beta sample.

References

1 C. Y. Lee, J. Wen, S. Thomas, W. Nicholas Delgass, J. B. Grutzner, G. T. Tsao, *Appl. Biochem. Biotechnol.* 1995**, 51**, 29-41.

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