Catalytic Production of Hexane-1,2,5,6-tetrol from Bio-renewable Levoglucosanol in Water: Effect of Metal and Acid Sites on (Stereo)-Selectivity

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8. Supplemental Information

8.1 ^{13}C NMR of reaction products

8.1.1. DDM and DDG

To assign the ^{13}C NMR spectra of DDG and DDM, we first determined that there were four different chemical species (based on comparison of peak areas in the quantitative ^{13}C NMR; see Table S1). These compounds are assigned as α and β anomers of DDG and DDM. Different ratios of DDG and DDM were generated by converting lgol feedstocks over Amberlyst 70 at 100^{o}C with t/e ratios of 1.3 (Table 3, Entry 2) and 3.3 (Table 4, Entry 5). We calculated the peak area ratios of different pairs of these four peaks (e.g. [DDM_1 + DDM+2]/[DDG_1 + DDG_2]) and found that only one of these ratios matched the ratio of the two peaks observed in the HPLC, as well as the t/e ratio of the converted lgols (Table S2). We cannot rule out the possibility that the stereochemistry at the C_2 position is completely inverted upon lgol hydrolysis, but there is no chemical reason to expect this to occur. The α and β anomers were not distinguished in this study; these species are expected to exist in equilibrium in water. All assignments are in reasonable agreement with the Mestrenova ^{13}C NMR-predicted chemical shifts for DDM/DDG (Table S3), noting that DDM and DDG are not distinguished by the NMR prediction software. The multiplicities of each ^{13}C peak (Table S1) are consistent with the assignments. The C_2 and C_5 carbon positions were not distinguished due to their similar chemical shifts and multiplicities. The C_3 and C_4 positions were also not distinguished due to their similar chemical shifts and multiplicities.

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Table S1: *Quantitative ^{13}C NMR chemical shifts, relative peak areas, and multiplicities of reaction products of lgol conversion over Amberlyst 70 with two different t/e ratios at 100°C (Table 3, Entry 2 and Table 4, Entry 5). "DDG_1" and "DDG_2" refer to the two anomers of DDG, and "DDM_1" and DDM_2" refer to the two anomers of DDM. Residual lgol peaks were excluded from this table. Multiplicities were assigned based on ^{13}C DEPT135 and DEPT90 NMR experiments.*

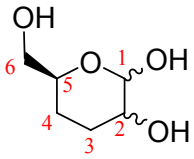
		Lgol t/e = 1.3 Feed	Lgol t/e= 3.3 feed			
#	Chemical Shift (ppm)	Normalized Area	Normalized Area	Multiplicity	Assignment	Carbon Position
1	98.19 .. 98.12	100	100	C-H	DDG_1	C1
2	94.97 .. 94.93	45	127	C-H	DDM_2	C1
3	93.45 .. 93.39	63	183	C-H	DDM_1	C1
4	91.90 .. 91.84	31	36	C-H	DDG_2	C1
5	76.79 .. 76.74	47	129	C-H	DDM_2	C2 or C5
6	76.68 .. 76.61	100	101	C-H	DDG_1	C2 or C5
7	70.39 .. 70.34	96	106	C-H	DDG_1	C2 or C5
8	69.47 .. 69.41	62	177	C-H	DDM_1	C2 or C5
9	68.73 .. 68.69	28	25	C-H	DDG_2	C2 or C5
10	67.84 .. 67.79	30	32	C-H	DDG_2	C2 or C5
11	66.14 .. 66.09	46	129	C-H	DDM_2	C2 or C5
12	65.73 .. 65.68	64	184	C-H	DDM_1	C2 or C5
13	64.39 .. 64.32	61	192	C-H2	DDM_1	C6
14	64.27 .. 64.22	44	135	C-H2	DDM_2	C6
15	63.98 .. 63.94	27	30	C-H2	DDG_2	C6
16	63.90 .. 63.83	101	110	C-H2	DDG_1	C6
17	29.45 .. 29.37	100	114	C-H2	DDG_1	C3 or C4
18	27.92 .. 27.85	39	140	C-H2	DDM_2	C3 or C4
19	25.81 .. 25.75	100	102	C-H2	DDG_1	C3 or C4
20	25.45 .. 25.41	31	38	C-H2	DDG_2	C3 or C4
21	24.37 .. 24.33	27	30	C-H2	DDG_2	C3 or C4
22	23.53 .. 23.47	64	177	C-H2	DDM_1	C3 or C4
23	20.42 .. 20.36	66	181	C-H2	DDM_1	C3 or C4
24	20.06 .. 20.00	48	134	C-H2	DDM_2	C3 or C4

	Lgol t/e = 1.3 Feed		Lgol t/e= 3.3 feed	
Species	Average Peak Area	Standard Error (%)	Average Peak Area	Standard Error (%)
DDG_1	99	1%	106	2%
DDG_2	29	3%	32	6%
DDM_1	63	1%	182	1%
DDM_2	45	3%	132	1%

Table S2: *Ratio of DDM to DDG by ^{13}C NMR and by HPLC, and ratio of converted threo- and erythro- lgol isomers, for hydrolysis of lgol using two different lgol diastereomer ratios (1.3 and 3.3).*

t/e Lgol Feed	DDM/DDG (NMR)	DDM/DDG (HPLC)	t/e Converted Lgol
1.3	0.82	0.89	0.92
3.3	2.3	2.2	2.4

Table S3: *Mestrenova ^{13}C NMR-predicted chemical shifts (ppm) for DDM/DDG (which are not distinguished in the NMR prediction). The carbon numbering convention is also provided.*



DDM & DDG

Carbon Position	DDM & DDF
1	97.3
2	70.3
3	26.7
4	25.2
5	73.3
6	65.3

8.1.2. DDF

DDF was produced from treatment of lgol in water over SiAl at 150°C (Table 1, Entry 7). The quantitative ^{13}C NMR assignments of the different tautomers of DDF are shown in Table S4. Similar to fructose, five tautomers are observed by ^{13}C NMR: acyclic ketone, α and β- furanose, and α and β-pyranose. The ketone tautomer was assigned based on the observation a ketone peak at 213.7 ppm (quaternary), and the C_5 carbon position ("C-H" multiplicity) at 71.1 ppm. The α and β furanose tautomers were assigned based on the two peaks at 106.4 and 106.0 ppm (C_2 anomeric carbon; quaternary), and two peaks at 81.5 and 79.6 ppm (C_5 hydroxymethyl-ether carbon; "C-H" multiplicity). The C_5 hydroxymethyl-ether carbon position is only present in the furanose tautomer, allowing the furanose and pyranose tautomers to be distinguished. The C_2 anomeric carbon positions of the α and β pyranose tautomers were assigned as the two peaks at 95.7 and 95.1 ppm. The α and β anomers were not distinguished in this study.

Concerning the region of the ^{13}C NMR spectrum of DDF up-field of 70 ppm, peaks corresponding to the different tautomers of DDF could not be completely distinguished due to the similar chemical shifts between different carbon positions. As shown in Table S4, the chemical shift, relative peak area, and multiplicity of each carbon position are consistent with the assignments; all assignments are also in reasonable agreement with the Mestrenova ^{13}C NMR predicted chemical shifts (Table S5). In the region of the spectrum between 63-68 ppm, the expected number of "pyranose (C_1 or C_6)" peaks (four), "pyranose (C_5)" peaks (two), and "ketone or furanose (C_1 or C_6)" peaks (six) are observed. The C_5 pyranose peak was assigned based on the "C-H" multiplicity of this carbon position. The C_1 and C_6 carbon positions of the ketone and furanose tautomers were not distinguished because the peaks had similar chemical shifts, peak areas, and multiplicities. In the region of the spectrum between 23-34 ppm, the expected number of "ketone or furanose (C_3 or C_4)" peaks (six) and the expected number of pyranose (C_3 or C_4) peaks (four) are observed. The C_3 and C_4 carbon positions of the ketone and

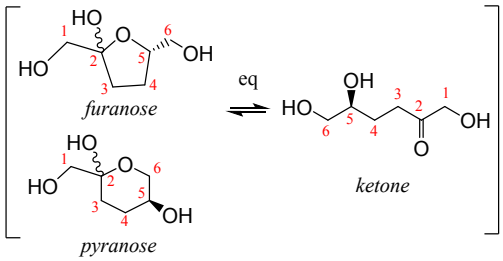
furanose tautomers were not distinguished because the peaks had similar chemical shifts, peak areas, and multiplicities.

Table S4*: Quantitative ^{13}C NMR chemical shifts, normalized peak areas, multiplicities, and assignments from quantitative-^{13}C NMR of reaction products of lgol conversion over SiAl at 150^{o}C (similar to Table 1, Entry 7). Multiplicities were assigned based on ^{13}C DEPT135 and DEPT90 NMR experiments. "Assignments" refers to the assignment of the carbon position for a given tautomer (ketone, furanose, or pyranose) of DDF. Minor peaks from residual lgol were excluded from this table.*

#	Chemical Shift (ppm)	Normalized Area	Multiplicity	Assignment
1	213.78 .. 213.73	100.0	Quaternary	Ketone (C2)
2	106.41 .. 106.33	111.7	Quaternary	Furanose (C2)
3	106.01 .. 105.96	79.2	Quaternary	Furanose (C2)
4	95.68 .. 95.64	44.4	Quaternary	Pyranose (C2)
5	95.15 .. 95.11	38.4	Quaternary	Pyranose (C2)
6	81.55 .. 81.50	78.5	C-H	Furanose (C5)
7	79.60 .. 79.55	94.8	C-H	Furanose (C5)
8	71.11 .. 71.05	94.1	C-H	Ketone (C5)
9	67.68 .. 67.62	40.6	C-H2	Pyranose (C1 or C6)
10	67.20 .. 67.13	89.1	C-H2	Ketone or furanose (C1 or C6)
11	67.02 .. 66.97	35.4	C-H2	Pyranose (C1 or C6)
12	65.35 .. 65.28	92.7	C-H2	Ketone or furanose (C1 or C6)
13	65.24 .. 65.16	99.0	C-H2	Ketone or furanose (C1 or C6)
14	65.14 .. 65.07	81.9	C-H2	Ketone or furanose (C1 or C6)
15	65.07 .. 65.02	42.4	C-H	Pyranose (C5)
16	64.90 .. 64.84	75.5	C-H2	Ketone or furanose (C1 or C6)
17	64.69 .. 64.64	42.6	C-H2	Pyranose (C1 or C6)
18	64.24 .. 64.19	35.9	C-H2	Pyranose (C1 or C6)
19	63.69 .. 63.62	142.3 (two peaks)	Larger peak: C-H2 Smaller peak: C-H	Larger peak: Ketone or furanose (C1 or C6) Smaller peak: Pyranose (C5)
20	33.97 .. 33.91	93.4	C-H2	Ketone or furanose (C3 or C4)
21	33.42 .. 33.36	81.6	C-H2	Ketone or furanose (C3 or C4)
22	33.07 .. 33.01	96.8	C-H2	Ketone or furanose (C3 or C4)
23	28.71 .. 28.65	46.4	C-H2	Pyranose (C3 or C4)
24	26.46 .. 26.41	47.6	C-H2	Pyranose (C3 or C4)
25	26.28 .. 26.21	95.7	C-H2	Ketone or furanose (C3 or C4)
26	25.86 .. 25.79	85.2	C-H2	Ketone or furanose (C3 or C4)
27	25.66 .. 25.58	104.8	C-H2	Ketone or furanose (C3 or C4)
28	24.10 .. 24.04	48.0	C-H2	Pyranose (C3 or C4)
29	23.89 .. 23.84	48.1	C-H2	Pyranose (C3 or C4)

Table S5: *Mestrenova ^{13}C NMR-predicted chemical shifts (ppm) for furanose, ketone, and pyranose tautomers of DDF. The carbon numbering convention is also provided.*

Carbon Position	Pyranose	Furanose	Ketone
1	66.4	66.8	69.1
2	95.4	103.9	212.1
3	30.0	32.1	36.6
4	27.4	27.4	29.0
5	67.2	74.5	71.6
6	66.7	65.9	66.8



DDF

Electrospray ionization mass spectrometry (ESI-MS) analysis of DDF was done on a Bruker maXis ultra-high resolution, time-of-flight mass spectrometer using infusion in positive ion mode. Samples were diluted 1:60,000 in 85% methanol/15% water (v/v) prior to analysis. Samples were infused at 3 uL/min with a source voltage of 3500V. The source temperature was set to 180°C while the nebulizer pressure was 0.4 bar and the drying gas flow was 4 L/min. The mass range measured was 75 to 1550 m/z. The ESI-MS shows a single major peak at m/z = 171, consistent with the molecular weight of DDF (148 g/mol) plus a sodium ion (23 g/mol). This result rules out the presence of a hydrated geminal diol (which would have molecular weight 166 g/mol), a compound which could also show a quaternary ^{13}C NMR peak in the 90-110 ppm region of the ^{13}C NMR spectrum. A smaller peak at m/z = 131 was observed, which could correspond to a protonated isomer of lgol (e.g. a THFDM precursor, 130 g/mol).

8.1.3. Tetrol

Cis- and trans- tetrol were assigned using reported ^{13}C NMR chemical shifts from the literature.[1] The c/t ratio was calculated based on the ratio of these peaks measured by quantitative ^{13}C NMR.

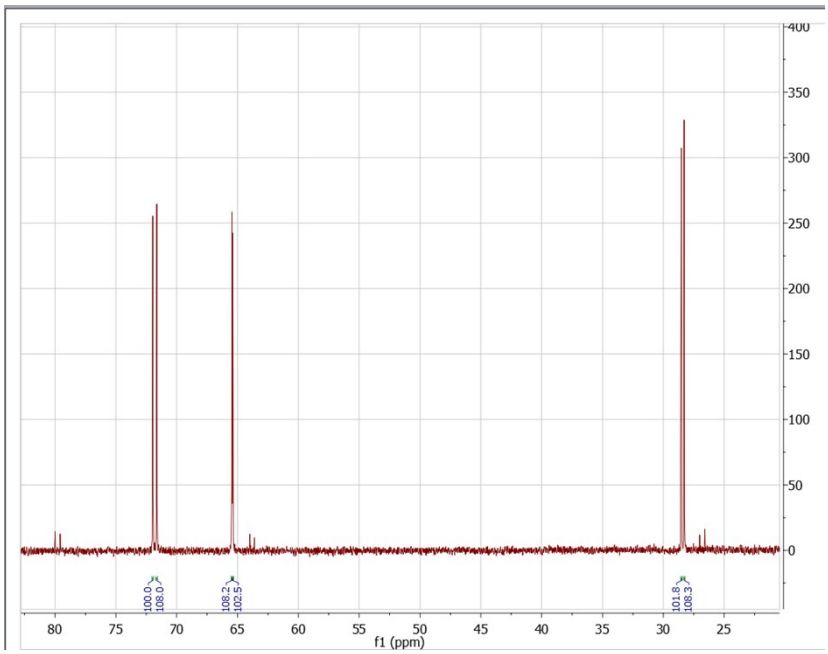


Figure S1: *Quantitative ^{13}C NMR of product of Tetrol, produced in Table 1, Entry 3. cis-tetrol: 71.7, 65.5, 28.3 ppm. trans-tetrol: 72.0, 65.4, 28.6 ppm. A small amount of side-product THFDM is also present in this spectrum, consistent with the GC results.*

8.2. HPLC Chromatograms of Reaction Products

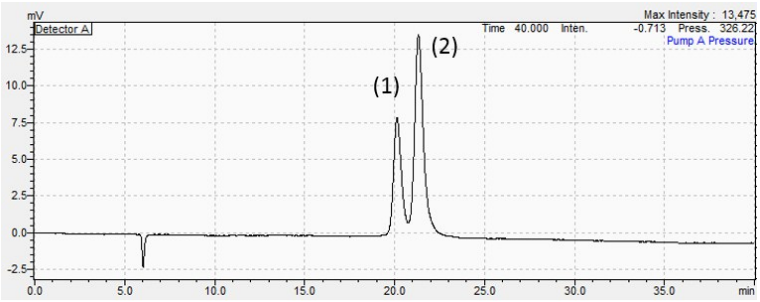


Figure S2_A: *Lgol (t/e = 1.3) feedstock. (1) = erythro-Lgol. (2) = threo-Lgol.*

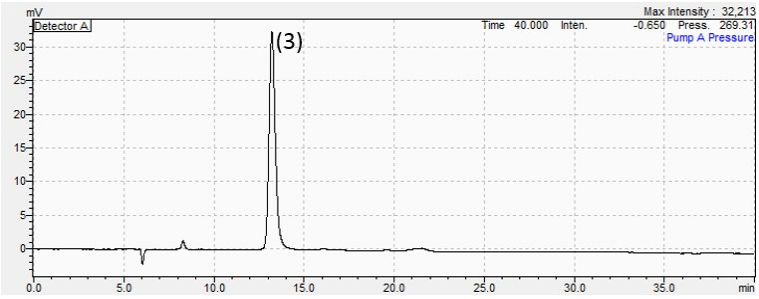


Figure S2_B: *Product of Table 1, Entry 3. (3) = mixture of cis- and trans-Tetrol. Minor unknown compound also observed at a retention time of 8 min.*

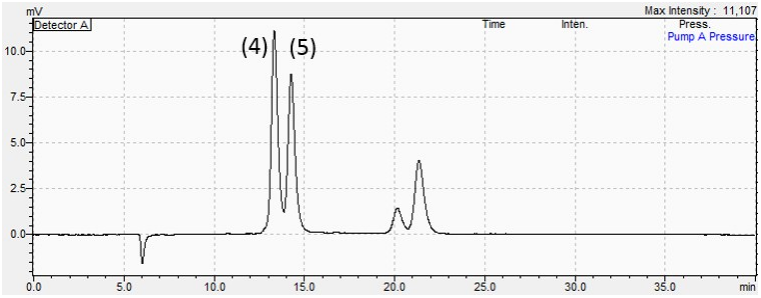


Figure S2_C: *Product of Table 3, Entry 2. (4) = DDG. (5) = DDM.*

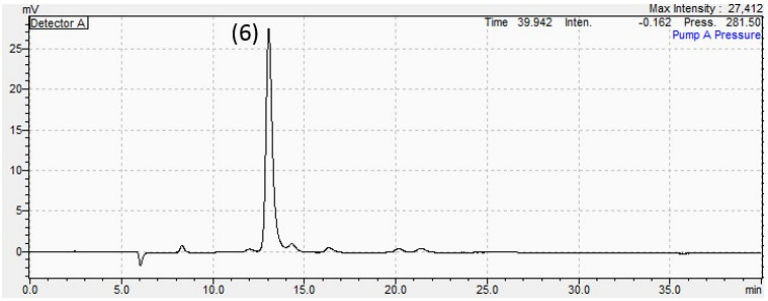
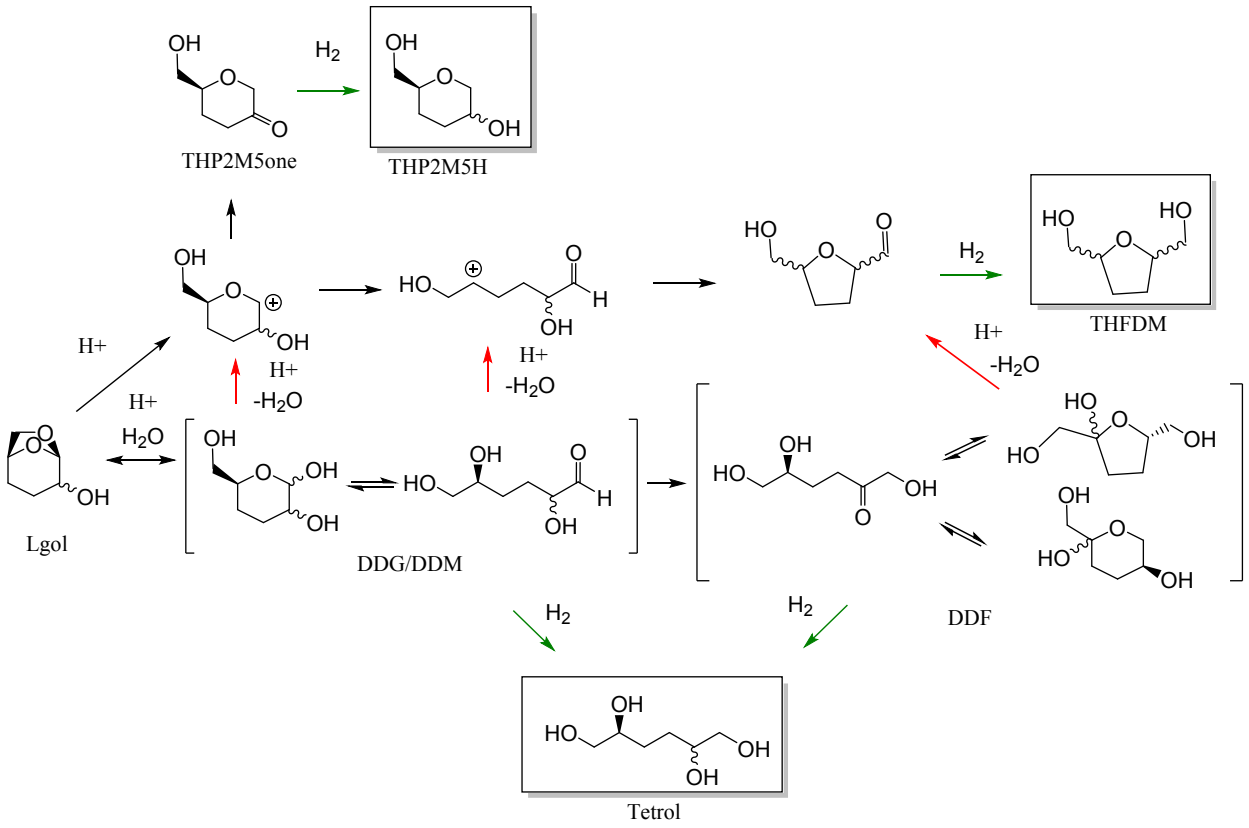


Figure S2_D: *Product of Table 1, Entry 7. (6) = DDF.*

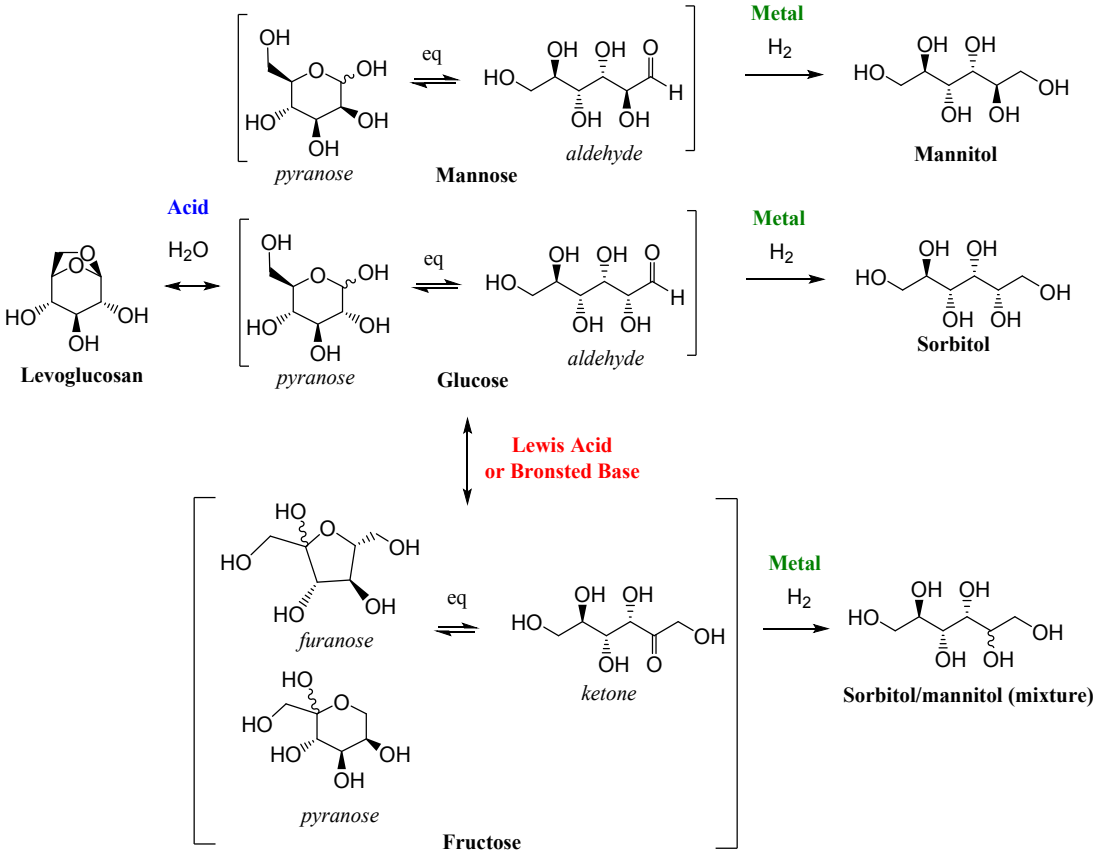
Figure S2: *HPLC chromatograms of reaction products. Compounds in the HPLC were assigned based on comparison with ^{13}C NMR spectra. DDG, DDF, cis-tetrol, and trans-tetrol are all overlapped in the HPLC.*

8.3. Comparison of proposed pathways of lgol conversion to tetrol, THFDM, and THP2M5H



Scheme S1: *Proposed pathways to form tetrol, THFDM, and THP2M5H from lgol. The pathway to form THFDM and THP2M5H from lgol in THF solvent was reported in our previous work.*[2] *Red arrows indicate hypothetical dehydration reactions which could connect the tetrol and THFDM production pathways. Green arrows indicate hydrogenation reactions occurring on metal sites.*

8.4. Reaction network for metal- and acid- catalyzed conversions of levoglucosan, mannose, glucose, and fructose



Scheme S2: *Relevant acid-catalyzed and metal-catalyzed reactions of levoglucosan, glucose, mannose, and fructose. "eq" indicates reactions which are assumed to be quasi-equilibrated.*

8.6. References for Supplemental Information

1. M. E. Maier and S. Reuter, *Liebigs Annalen*, 1997, 2043-2046.

2. S. H. Krishna, R. S. Assary, Q. A. Rashke, Z. R. Schmidt, L. A. Curtiss, J. A. Dumesic and G. W. Huber, *ACS Catalysis*, 2018, 3743-3753.