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Insight into the Dehydration of High-concentration Fructose to 5-Hydroxymethylfurfural in Oxygen-containing Polar Aprotic Solvents

Zuojun Wei, En Yao, Yuran Cheng, Jinbo Hu, and Yingxin Liu*

College of Pharmaceutical Science, Zhejiang University of Technology, 1 GongDa Road, Wukang Street, Deqing County, HuZhou 313200, P.R. China.

Email: yxliu@zjut.edu.cn

Table of contents

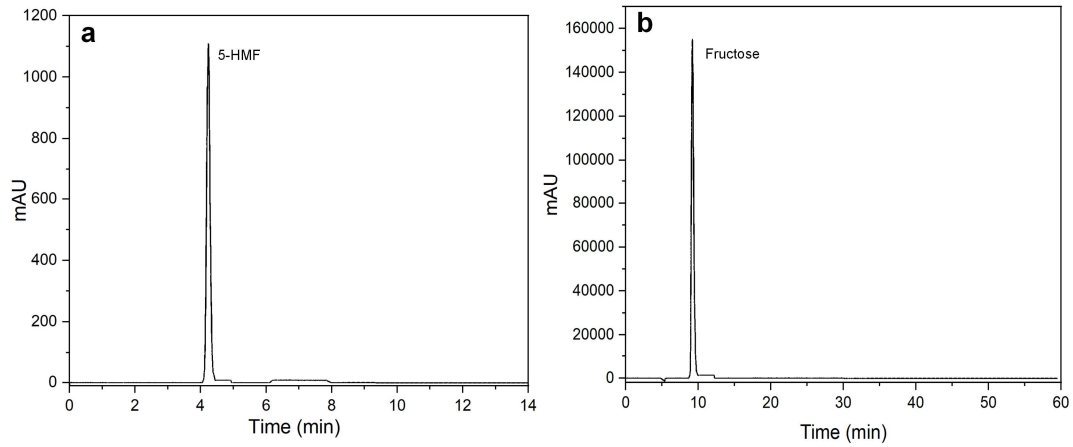


Fig. S1 Liquid chromatogram of a: 5-HMF and b: fructose.

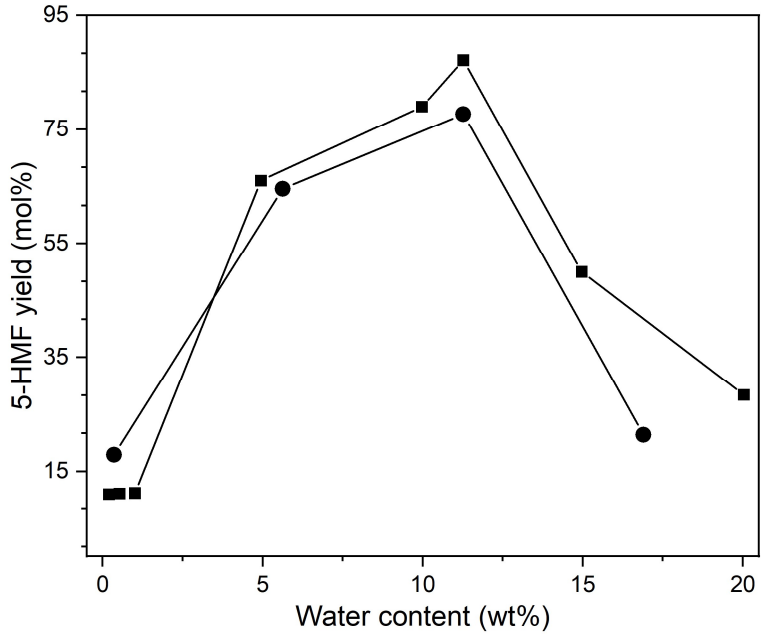


Fig. S2 Effect of water content on 5-HMF yield for 1 wt% and 20 wt% fructose concentration. Reaction conditions: ■: 1 wt% fructose concentration, ●: 20 wt% fructose concentration, n(HCl)/n(fructose) = 3.6%, 6.1 g 1,4-dioxane, 140 °C, 30 min, rotate speed: 1000 rpm.

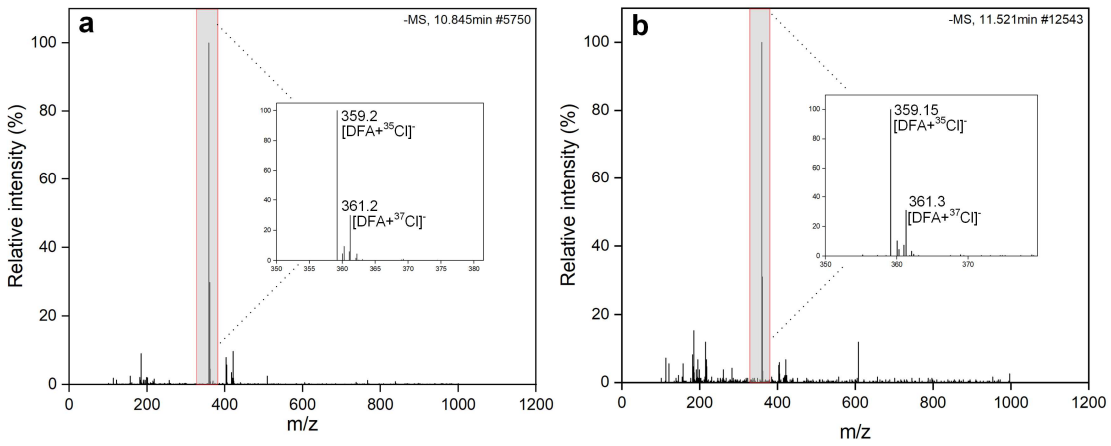


Fig. S4 Mass spectrum of unknown intermediate in reaction products a: RT. at 10.85 min and b: RT. at 12.20 min.

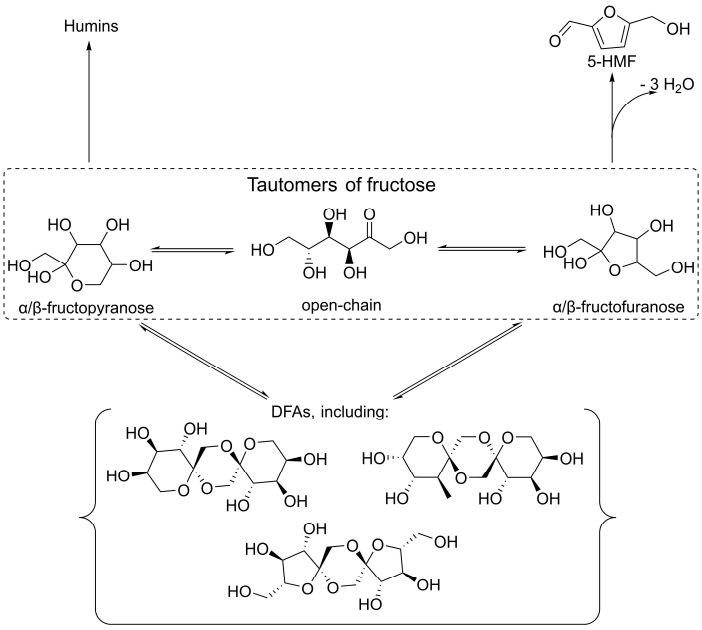
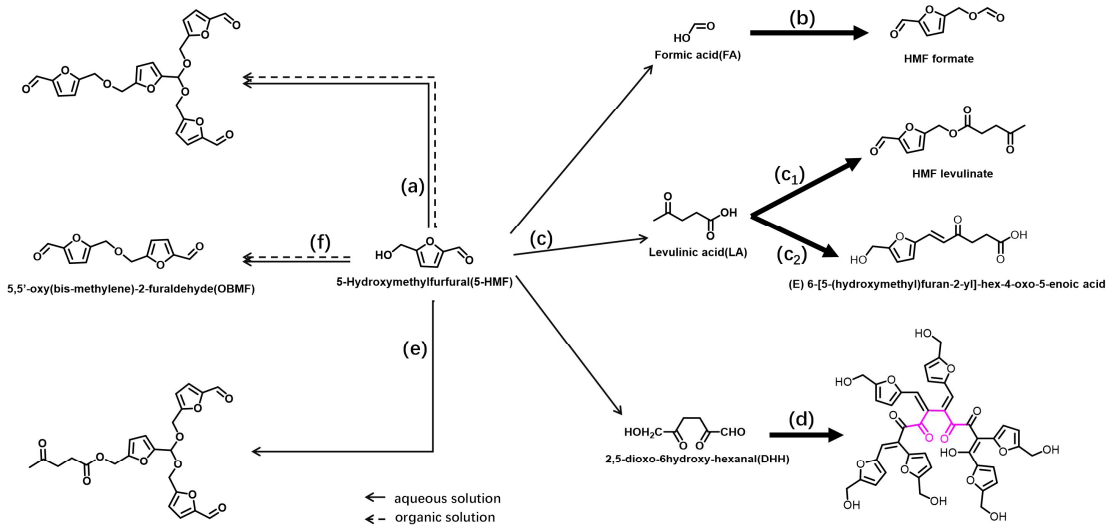


Fig. S5 Molecular isomers of fructose and their acid catalyzed dehydration to 5-HMF and DFAs.



Etherification: (a), (f); Acetalization: (a), (e); Esterification: (b), (c_1), (e); Aldol addition/condensation: (c_2), (d).

Fig. S6 Various pathways of the growth of humins via 5-HMF.[1,2]

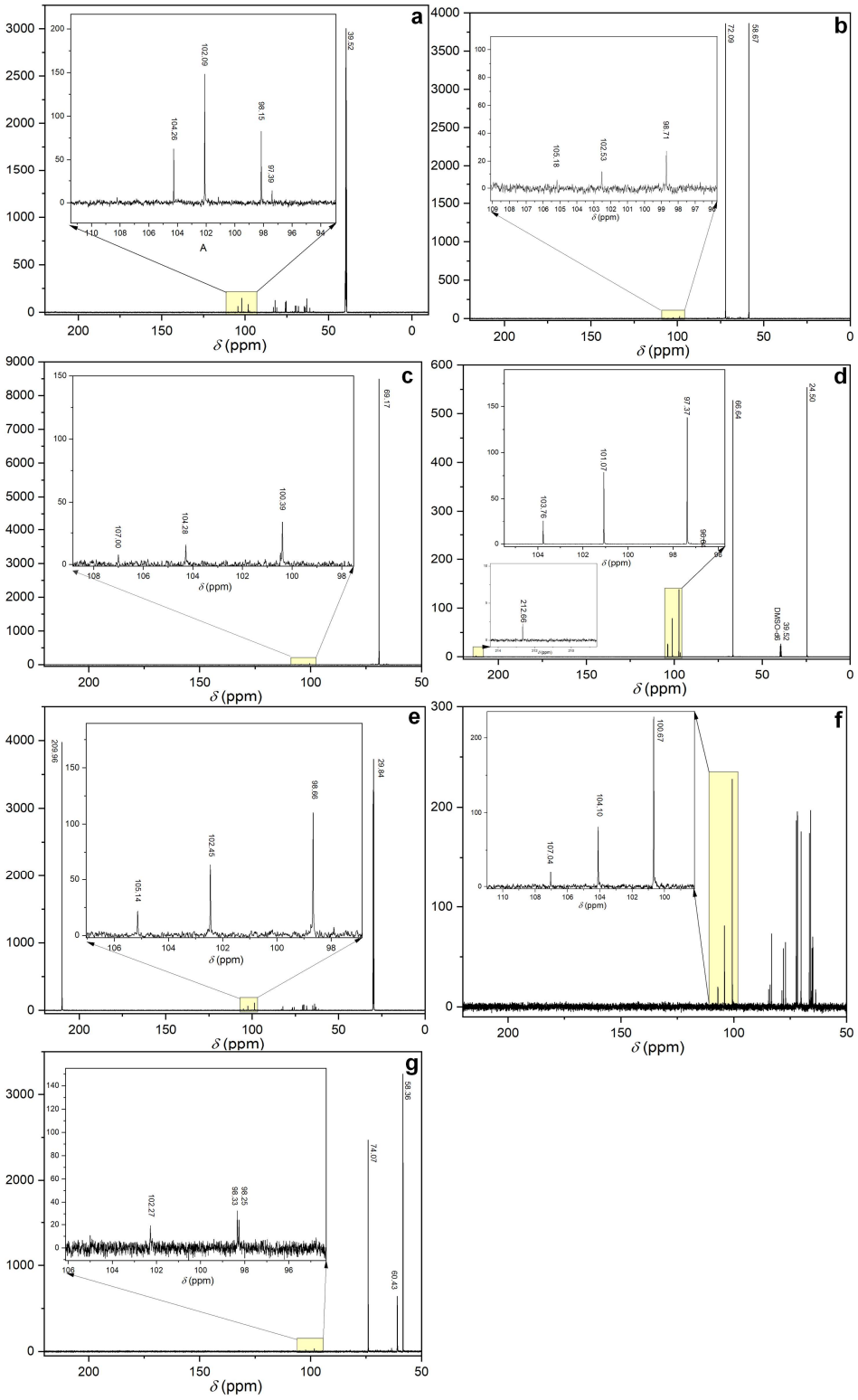


Fig. S7 ^{13}C-NMR of D-fructose in a: DMSO-d_6, b: EGDE:water (8:2), c: DIO:water (9:1), d: THF:water (8:2), e: ACE:water (8:2), f: D_2O, g: EGME:water (9:1) at 25 °C. Note: The addition of water is to make 20 mg of fructose be fully dissolved for NMR detection. For THF:water (8:2) mixture, only 10 mg fructose is soluble. We therefore used isotopic 2-^{13}C-labeled D-fructose instead to obtain satisfactory NMR signal.

Table S1 Peak area of DFAs and fructose

Reaction time (min)	HPLC Peaks								
	DFA1		DFA2		DFA3		Area sum of DFAs (mAU)	Fructose	
	R.T[b] (min)	Area (mAU)	R.T (min)	Area (mAU)	R.T (min)	Area (mAU)		R.T (min)	Area (mAU)
7	10.32	8680	10.90	30608	11.58	333	39621	12.22	880899
9	10.38	130796	10.89	10692	11.53	6398	147886	12.22	824400
11	10.39	260711	10.85	256134	11.53	74512	591357	12.26	320102
13	10.38	495577	10.84	600081	11.59	88333	1183991	12.25	87721
15	10.32	6805	10.90	6104	11.58	769	13678	12.22	52342

[a] R.T: retention time.

Table S2 Tautomer distributions of fructose in various solvents at room temperature

Entry	Solvent	Fructofuranose	Fructopyranose	Open chain	5-HMF yield (%)	References
1	D_2O	32.7	67.3	trace	19.0	This work
2	EGME (9:1)	27.9	72.1	trace	61.4	This work
3	ACE (8:2)	43.0	57.0	trace	71.5	This work
4	DIO (9:1)	38.4	61.5	trace	77.7	This work
5	EGDE (8:2)	45.9	54.1	trace	74.1	This work
6	THF (8:2)	47.0	52.1	0.9	78.3	This work
7	DMSO	69.0	31.0	trace	80.3	This work
1a	H_2O	25.6	74.4	trace	28.0	Ref. 3
1b	D_2O	29.3	70.0	0.7	NM.	Ref. 4
4a	ACE (9:1)	47.7	52.3	trace	76.2	Ref. 3
6a	THF 4:1)	33.0	66.0	1.0	58.5	Ref. 4
6b	THF (4:1)	44.7[b]	52.1[b]	3.2[b]	74.4	Ref. 4
7a	DMSO (9:1)	53.0	45.3	1.7	91.0	Ref. 4
7b	DMSO-d_6	65.6	32.0	2.4	80.0	Ref. 5
7c	DMSO-d_6	64.0	36.0	trace	NM.	Ref. 6
7d	DMSO-d_6	68.3	31.7	trace	NM.	Ref. 3
8	DHMTHF (9:1)	37.7	60.50	1.8	60.9	Ref. 4
9	DMF	56.0	43.0	trace	92.6	Ref. 7
10	GVL (20:3)	38.3	61.7	trace	69.0	Ref. 8
11	ethanol (9:1)	48.3	50.6	1.1	53.3	Ref. 4
11a	ethanol (9:1)	46.3[b]	51.0[b]	2.7[b]	47.5	Ref. 4
12	THFA (9:1)	33.1	58.4	1.5	54.3	Ref. 4

[a] NM: Not mentioned. [b] Detected at 60 °C

Reaction conditions:

Tucker's research[4]: 2 wt% fructose, Amberlyst 70 catalyst, 130 °C, THF: 6a: 20 min; 6b: 35 min; DMSO: 7a: 32 min; 2,5-(dihydroxymethyl)tetrahydrofuran:water (9:1 v:v): 8: 35 min; ethanol (9:1 v:v): 11: 30 min, 11a: 20 min; THFA (9:1 v:v): 12: 20 min.

Bicker's research[3]: 1 wt% fructose,10 mmol/L H_2SO_4, 180 °C, water: 1a: 25 MPa, 600 s; acetone: 4a: 20 MPa, 120 s.

Liu's research[7]: 5.5wt% fructose, mixed acid catalyst (H_2SO_4/H_3PO_4 = 1.0, $AlCl_3/(H_2SO_4+H_3PO_4)$ = 0.22), DMF 9: 120 °C, 20min.

Qi's research[8]: 3 wt% fructose, 0.075 mL H_2SO_4 (5mol/L), 0.5 mL GVL 10: 130 °C, 2 min.

Akien's research[5]: 9 wt% fructose, 0.01 mol/L H_2SO_4, 0.5 mL DMSO, 7b:120 °C, 120 min.

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