

Supporting Information

Borate-Stabilized Transformation of C6 Aldose to C4 Aldose

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Materials. D-(+)-Mannose (MAN, 99%), D-(+)-Glucose (GLU, 99.5%), D-(−)-Fructose (FRU, 99%), D-(−)-Erythrose (ERO, 75%), L-(+)-Erythrulose (ERU, 85%), Glycolaldehyde (GA) dimer were purchased from sigma-aldrich. Methanol for HPLC, Ethanol for HPLC, Isopropanol for HPLC, Sodium tetraborate decahydrate (99.5%), Molybdenum(VI) oxide (MoO_3), Tin(IV) chloride pentahydrate (99%) were purchased from Sinopharm Chemical Reagent Company. Commercial β zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$) was purchased from Sinopec Shanghai Research Institute of Petrochemical Technology. Deionized water was produced by a laboratory water purification system.

Methods.

Preparation of Sn- β catalyst. Sn- β catalyst was prepared by post-treatment method.^[1] In typical, 1 g of commercial β zeolite ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 25$) was dealuminated by stirring in 55 mL of aqueous nitric acid solution (7.2 mol L^{-1}) at 80°C for 8 h. Afterwards, the solids were filtered, washed with deionized water and dried at 60°C . Before the grafting of tin, the solids were activated overnight at 170°C to remove physisorbed water. Next, the sample was suspended in 100 mL of isopropanol and 27 mmol of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$ was added. The solution was refluxed under N_2 for 5 h and then filtered, rinsed with isopropanol and dried at 60°C . Finally, the solids were calcined at 550°C for 6 h.

Retro-aldol process of C6 aldoses into GA and ERO. The catalytic reactions were carried out in a 30 mL thick-walled glass reactor and the reaction mixtures were heated by microwave irradiation. Briefly, 100 mg of C6 aldoses (MAN or GLU) were dissolved in 5 g of methanol (or ethanol) with/without 53 mg of sodium borate. And then 12 mg of MoO_3 catalyst was added and the mixture was dispersed uniformly by ultrasonic. After that, the glass reactor containing reaction mixture was put into microwave instrument (Anton Paar Monowave 300) and heated to desired temperature. After reacting for a certain time with magnetic stirring, the reactor was cooled by compressed air.

Aldol condensation of GA into ERO and hexose. The catalytic reactions were carried out in a 30 mL thick-walled glass reactor and the reaction mixtures were heated by microwave irradiation. Typically, 100 mg of GA was dissolved in 5 g of methanol with/without 53 mg of sodium borate. And then 12 mg of MoO_3 catalyst was added and the mixture was dispersed uniformly by ultrasonic. After that, the glass reactor containing reaction mixture was put into microwave instrument and heated to desired temperature. After reacting for a certain time with magnetic stirring, the reactor was cooled by compressed air.

One-pot two-step cascade conversion of MAN into ERU. The reaction procedures for converting MAN into ERO are the same as the above processes. After MoO_3 solid was removed by centrifugation, 10 mL of isopropanol was added into the reaction mixture. On this occasion, sodium borate was fast precipitated and removed because of its extremely low solubility in isopropanol. Then the obtained solution was taken onto a rotary evaporator to remove methanol and part of isopropanol. The solution was concentrated to about 5 mL, and 50 mg of Sn- β was added. Finally, the reaction was taken at 100°C for 60 min under microwave irradiation.

Product analysis. The reaction solution of 100 μL was taken out and diluted to 1000 μL with deionized water. The samples were analyzed on high performance liquid chromatography (HPLC, Shimadzu Corporation) equipped with refractive index detector (RID). The reaction products were separated using Shodex SC1011 sugar column at 80°C with deionized water ($\text{pH} = 7.0$) as the mobile phase at the flow rate of 0.6 mL min^{-1} . Before being injected into HPLC the samples needed to be filtered through a micro syringe filter (VWR, $0.2 \mu\text{m}$ PES). The retention times of detectable

sugars were as follows: GLU (12.4 min), MAN (13.8 min), FRU (14.7 min), GA (16.2 min), ERU (17.2 min) and ERO (22.2 min). High-resolution mass spectra of reaction products were recorded on Bruker McrOTOF II mass spectrometer. ¹¹B-NMR and ¹³C-NMR of solutions were recorded on Bruker AVANCE III HD 500 MHz spectrometer.

For the retro-aldol condensation of hexose into GA and ERO, conversion of substrate and carbon yield of products were calculated as follows:

$$Conv_{\text{hexose}} = \left[1 - \frac{\text{Mole of hexose in the product}}{\text{Initial mole of hexose}} \right] \times 100\%$$

$$Y_{\text{GA}} = \frac{1}{3} \times \frac{\text{Mole of GA in the product}}{\text{Initial mole of hexose}} \times 100\%$$

$$Y_{\text{ERO}} = \frac{2}{3} \times \frac{\text{Mole of ERO in the product}}{\text{Initial mole of hexose}} \times 100\%$$

$$Y_{\text{ERU}} = \frac{2}{3} \times \frac{\text{Mole of ERU in the product}}{\text{Initial mole of hexose}} \times 100\%$$

$$Y_{\text{GLU}} = \frac{\text{Mole of GLU in the product}}{\text{Initial mole of hexose}} \times 100\%$$

$$Y_{\text{FRU}} = \frac{\text{Mole of FRU in the product}}{\text{Initial mole of hexose}} \times 100\%$$

$$Y_{\text{MAN}} = \frac{\text{Mole of MAN in the product}}{\text{Initial mole of hexose}} \times 100\%$$

$$Conv_{\text{retro-aldol}} = Conv_{\text{MAN}} - Y_{\text{GLU}} - Y_{\text{FRU}} \quad (\text{for MAN conversion reaction})$$

$$Conv_{\text{retro-aldol}} = Conv_{\text{GLU}} - Y_{\text{MAN}} - Y_{\text{FRU}} \quad (\text{for GLU conversion reaction})$$

For the aldol condensation of GA toward ERO and C6 sugars, conversion of substrate and carbon yield of products were calculated as follows:

$$Conv_{\text{GA}} = \left[1 - \frac{\text{Mole of GA in the product}}{\text{Initial mole of GA}} \right] \times 100\%$$

$$Y_{\text{ERO}} = 2 \times \frac{\text{Mole of ERO in the product}}{\text{Initial mole of GA}} \times 100\%$$

$$Y_{\text{C6}} = 3 \times \frac{\text{Mole of C6 sugars in the product}}{\text{Initial mole of GA}} \times 100\%$$

For the conversion of ERO into ERU, the yield of ERU was calculated as follows:

$$Y_{\text{ERU}} = \frac{\text{Mole of ERU in the product}}{\text{Initial mole of ERO}} \times 100\%$$

The total carbon yield of ERU from MAN was calculated by $Y_{\text{ERU}} \times Y_{\text{ERO}}$.

Conv.: Conversion, Y.: Yield. GA: glycolaldehyde, ERO: erythrose, ERU: erythrulose, GLU: glucose, FRU: fructose, MAN: mannose.

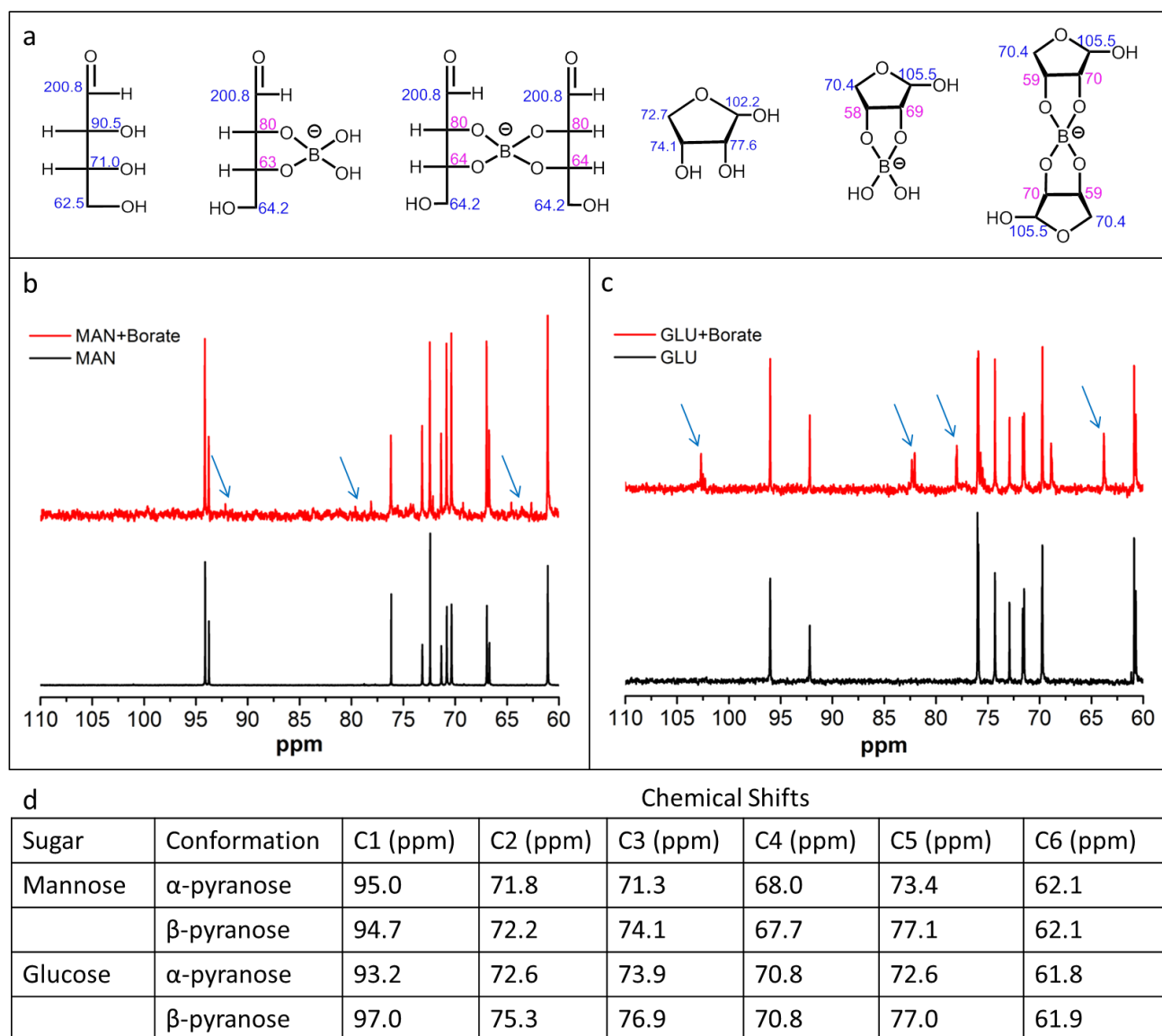


Figure S1. (a) Predict ^{13}C NMR shifts of ERO and ERO-borate complexes in different structures. The shift values are obtained from ChemDraw software. (b) ^{13}C NMR spectra of MAN (black line) and borate-containing MAN with a boron/MAN mole ratio of 1/1 (red line) in H_2O . (c) ^{13}C NMR spectra of GLU (black line) and borate-containing GLU with a boron/GLU mole ratio of 1/1 (red line) in H_2O . (d) ^{13}C NMR shifts of MAN and GLU in different conformations^[2].

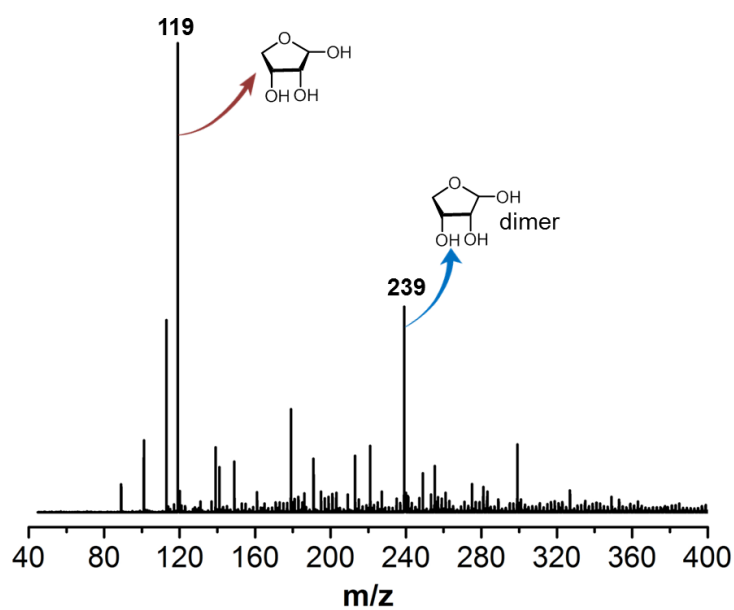


Figure S2. MS analysis result of ERO product separated from reaction solution of MAN conversion. Reaction condition: 100 mg of MAN, 53 mg of sodium borate and 12 mg of MoO_3 were added into 5 g of methanol and reactions were taken at 150 °C for 15 s.

Table S1. Specific optical rotation of ERO solution.^[a]

Sample	$[\alpha]^{20}_{\text{D}}$
Commercial ERO dissolved in water	-15.6°
Prepared ERO dissolved in water ^[b]	-16.9°
Commercial ERO dissolved in methanol	-9.4°
Commercial ERO and borate dissolved in methanol	-16.7°

[a] The concentration of all the solution is fixed at 1.0 wt%. [b] ERO prepared from MAN in methanol containing borate and MoO₃ is separated from reaction mixture by HPLC (column SC1011), and concentrated by freeze drying process.

Table S2. Influence of borate on MAN conversion in methanol by using MoO₃ as catalyst.^[a]

Boron/MAN (mole ratio)	Time [s]	Conv. _{retro-aldol} [mol%]	Yield [C mol%]			Carbon balance [mol%] ^[b]
			C2	C4		
			GA	ERO	ERU	
1/4	5	29.6	3.0	14.9	0.0	88.3
	15	37.7	4.6	14.7	0.0	81.6
	30	45.2	5.5	14.6	0.0	74.9
1/2	5	30.7	3.3	21.0	0.0	93.6
	15	45.4	4.7	20.0	0.0	79.3
	30	51.4	5.7	19.1	0.0	73.4
3/4	5	25.8	2.7	22.5	0.0	99.4
	15	42.8	4.2	23.7	0.0	85.1
	30	54.9	5.2	21.3	0.0	71.6
1/1	5	33.0	2.6	23.0	0.0	92.6
	15	39.7	3.4	25.5	0.0	89.2
	30	46.7	4.0	22.2	0.0	79.5
5/4	5	32.1	2.6	24.7	0.0	95.2
	15	52.1	4.2	24.1	0.0	76.2
	30	72.1	5.0	19.4	0.0	52.3
3/2	5	46.3	3.0	24.9	0.0	81.6
	15	70.5	4.4	20.5	0.0	54.4
	30	80.0	5.0	15.9	0.0	40.9

[a] Reaction condition: 100 mg of MAN, 13~79 mg of sodium borate and 12 mg of MoO₃ were added into 5 g of methanol and reactions were taken at 150 °C for different time.

[b] Carbon balance is calculated by $[Y_{GA} + Y_{ERO} + Y_{ERU} + (1 - \text{Conv.}_{\text{retro-aldol}})]$. Conv.: Conversion, Y.: Yield, GA: glycolaldehyde, ERO: erythrose, ERU: erythrulose, MAN: mannose.

Table S3. Conversion results of MAN in ethanol with or without borate using MoO₃ as catalyst.

Solvent	Time [min]	Conv. _{retro-aldol} [mol%]	Yield [C mol%]			Carbon balance [mol%] ^[c]
			C2	C4		
			GA	ERO	ERU	
Ethanol ^[a]	5	22.5	1.8	13.4	0.0	92.7
	10	39.6	4.0	14.5	1.3	80.2
	15	53.5	7.4	8.9	2.5	65.3
Ethanol (borate) ^[b]	1	25.7	3.2	17.1	2.1	96.7
	3	37.6	5.6	21.2	3.3	92.5
	5	42.5	6.5	21.1	3.9	89.0

[a] Reaction condition: 100 mg of MAN and 12 mg of MoO₃ were added into 5 g of ethanol and reactions were taken at 150 °C for different time.

[b] Reaction condition: 100 mg of MAN, 10 mg of sodium borate and 12 mg of MoO₃ were added into 5 g of ethanol and reactions were taken at 150 °C for different time.

[c] Carbon balance is calculated by $[Y_{GA} + Y_{ERO} + Y_{ERU} + (1 - \text{Conv.}_{\text{retro-aldol}})]$. Conv.: Conversion, Y.: Yield, GA: glycolaldehyde, ERO: erythrose, ERU: erythrulose, MAN: mannose.

Table S4. Influence of MoO₃ on MAN conversion in methanol containing sodium borate.^[a]

MoO ₃ /MAN (weight ratio)	Time [s]	Conv. _{retro-aldol} [mol%]	Yield [C mol%]			Carbon balance [mol%] ^[b]
			C2	C4		
			GA	ERO	ERU	
0/100	5	1.2	0.0	0.0	0.0	98.8
	15	10.3	0.9	0.0	0.0	90.6
	30	16.5	1.2	0.0	0.0	84.7
	45	16.7	1.3	1.6	0.0	86.2
6/100	5	24.8	2.6	21.9	0.0	99.7
	15	49.9	4.4	24.6	0.0	79.1
	30	55.9	5.5	22.3	0.0	71.9
	45	64.6	5.6	18.1	0.0	59.1
12/100	5	30.0	3.2	25.9	0.0	99.1
	15	48.5	4.9	25.5	0.0	81.9
	30	61.5	5.8	21.2	0.0	65.5
	45	73.4	6.1	17.7	0.0	50.4
24/100	5	36.4	3.1	23.3	0.0	90.0
	15	55.6	4.8	21.9	0.0	71.1
	30	67.5	5.6	18.5	0.0	56.6
	45	73.8	6.0	16.3	0.0	48.5

[a] Reaction condition: 100 mg of MAN, 53 mg of sodium borate and 0~24 mg of MoO₃ were added into 5 g of methanol and reactions were taken at 150 °C for different time.

[b] Carbon balance is calculated by $[Y_{GA} + Y_{ERO} + Y_{ERU} + (1 - \text{Conv.}_{\text{retro-aldol}})]$. Conv.: Conversion, Y.: Yield, GA: glycolaldehyde, ERO: erythrose, ERU: erythrulose, MAN: mannose.

Table S5. Influence of MAN concentration on its conversion in methanol containing sodium borate by using MoO₃ as catalyst.^[a]

MAN concentration [wt%]	Time [s]	Conv. _{retro-aldol} [mol%]	Yield [C mol%]			Carbon balance [mol%] ^[b]
			C2	C4		
			GA	ERO	ERU	
1.0	5	41.2	5.5	25.4	0.0	89.7
	15	60.0	7.9	23.0	0.0	70.9
	30	72.9	8.2	17.9	0.0	53.2
2.0	5	30.0	3.2	25.9	0.0	99.1
	15	48.5	4.9	25.5	0.0	81.9
	30	61.5	5.8	21.2	0.0	65.5
5.0	5	28.2	1.2	16.9	0.0	89.9
	15	49.2	2.4	21.5	0.0	74.7
	30	62.3	3.3	18.6	0.0	59.6
10.0	5	25.9	0.5	10.2	0.0	84.8
	15	40.6	1.2	17.0	0.0	77.6
	30	50.7	1.8	16.6	0.0	67.7

[a] Reaction condition: 50~500 mg of MAN, a certain amount of sodium borate with a fixed boron/MAN mole ratio of 1/1, and MoO₃ with a fixed MoO₃/MAN weight ratio of 12/100 were added into 5 g of methanol, and reactions were taken at 150 °C for different time.

[b] Carbon balance is calculated by $[Y_{GA} + Y_{ERO} + Y_{ERU} + (1 - \text{Conv.}_{\text{retro-aldol}})]$. Conv.: Conversion, Y.: Yield, GA: glycolaldehyde, ERO: erythrose, ERU: erythrulose, MAN: mannose.

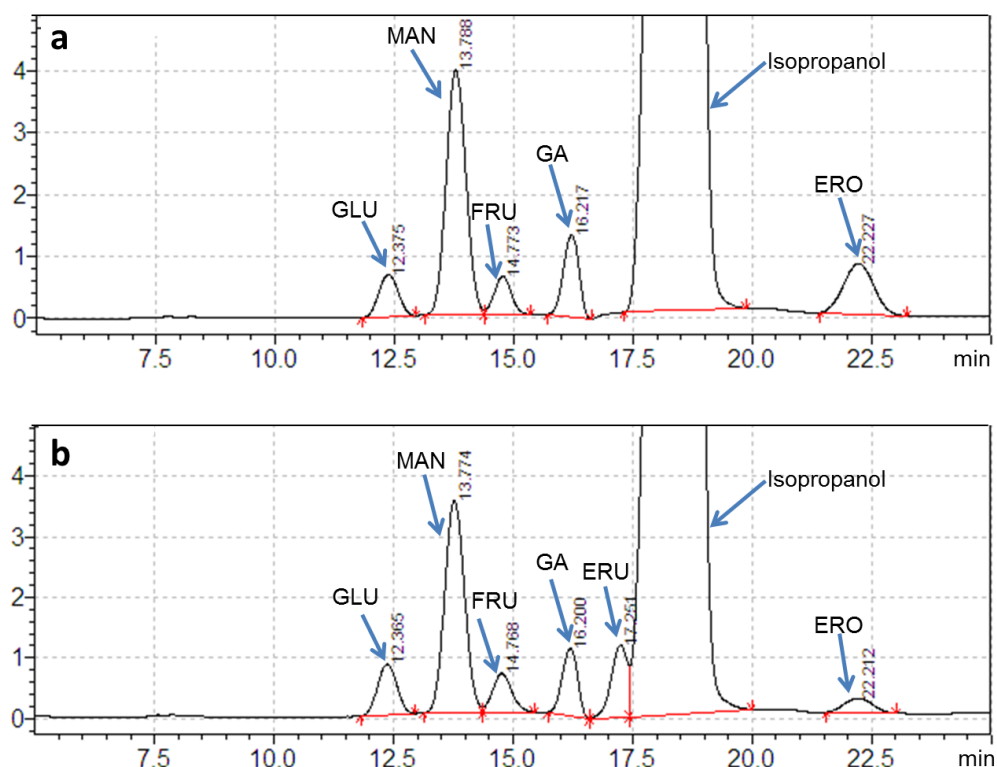


Figure S3. HPLC results of reaction solutions before (a) and after (b) the $\text{Sn-}\beta$ catalyzed isomerization process in isopropanol. GLU: glucose, FRU: fructose, MAN: mannose, GA: glycolaldehyde, ERU: erythrulose, ERO: erythrose.

The HPLC results clearly show the decrease of ERO and the appearance of ERU in isopropanol containing $\text{Sn-}\beta$, demonstrating the effective aldose-ketose interconversion from ERO to ERU. Sodium borate will be removed when the solvent is changed from methanol to isopropanol owing to the poor solubility of borate in isopropanol, and so ERO can be released from the borate-ERO complex and isomerization reaction occurs. Meanwhile, these results also indicate that the isomerization/epimerization process among glucose, fructose and MAN takes place since their peak areas change before and after reaction.

References

- [1] Dijkmans, J.; Gabriëls, D.; Dusselier, M.; de Clippel, F.; Vanelderen, P.; Houthoofd, K.; Malfliet, A.; Pontikes, Y.; Sels, B. F. *Green Chem.* **2013**, *15*, 2777-2785.
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