

Electronic supplementary information

Synthesis of *p*-Menthane-3,8-diol from Citronellal over Lignin-Derived Carbon Acid Catalysts

Irwan Kurnia ^a, Akihiro Yoshida ^{*a,b}, Nichaboon Chaihad ^a, Tirta Prakoso ^c, Shasha Li ^d, Xiao Du ^e, Xiaogang Hao ^e, Abuliti Abudula ^a, Guoqing Guan ^{*a,b}

^a *Graduate School of Science and Technology, Hirosaki University, 1 Bunkyocho, Hirosaki 036-8560, Japan*

^b *Energy conversion engineering Laboratory, Institute of Regional Innovation (IRI), Hirosaki University, 2-1-3 Matsubara, Aomori 030-0813, Japan. E-mail addresses: guan@hirosaki-u.ac.jp (G. Guan), ayoshida@hirosaki-u.ac.jp (A. Yoshida); Tel.: +81-17-762-7756; Fax: +81-17-735-5411.*

^c *Department of Chemical Engineering, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132, Indonesia*

^d *College of Chemical and Biological Engineering, Taiyuan University of Science and Technology, Taiyuan 030012, China*

^e *Department of Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China*

Table S1. The effect ratio of (\pm)-citronellal to AL-Py-500 carbon acid catalyst.

Entry	Ratio S/C ^a	Conv. (%)	Selectivity (%)		
			Isopulegol	PMD	Dimer
1	2:1	97	10	88	2
2 ^b	2:1	73	6	93	1
3	4:1	81	9	89	2
4	20:1	56	13	86	1
5 ^c	20:1	89	11	88	1

^aratio of (+)-citronellal to AL-Py-500 carbon acid catalyst; weight ratio of water to substrate (W/S = 25); reaction temp.: 50 °C; reaction time is 24 h; ^btreated by 0.1 M NaCl; ^creaction time of 72 h.

Table S2. Catalytic performance of the AL-Py-500 catalyst for cyclization-hydration reaction using different substrates.

Entry	Substrates	Conv. (%)	Yield ^d (mol %)		
			Isopulegol	PMD	Dimer
1 ^a	(\pm)-Citronellal	97	9	86	2
2 ^a	Isopulegol	<0.1	>99.9	<0.1	<0.1
3 ^b	Isopulegol	<0.1	>99.9	<0.1	<0.1
4 ^c	Isopulegol	<0.1	>99.9	<0.1	<0.1

^aweight ratio of substrate to AL-Py-500 catalyst (S/C = 2:1); weight ratio of water to substrate (W/S = 25); reaction temp.: 50 °C; reaction time: 24 h; ^breaction using 0.25 wt% H₂SO₄ and isopulegol with a weight ratio of 1:1 for 12 h reaction; ^creaction using 7 wt% citric acid and isopulegol with a weight ratio of 5:3 for 15 h reaction; ^dyield of the sum of isomers.

Table S3. Characterizations of commercial acid catalysts.

Catalyst	Total acid amount (mmol/g) ^a	Density of each acid functional group ^b		
		Carboxylic group	Lactonic group	Phenolic group
		(mmol/g)	(mmol/g)	(mmol/g)
CB	0.06	0.02	0.03	0.01
H-USY (Si/Al = 6)	0.61	-	-	-

^aacid-base back titration method with 0.01 M NaOH; ^bBoehm titration method with 0.01 M NaOH, 0.01 M NaHCO₃, and 0.01 M Na₂CO₃

Table S4. Reusability of AL-Py-500 catalyst for cyclization-hydration of (±)-citronellal.

Cycle number	Conv. (%)	Selectivity ^a (%)		
		Isopulegol	PMD	Dimer
Fresh	97	10	88	2
1 st	80	9	89	2
2 nd	78	9	90	1
3 rd	72	9	89	2

^athe sum of isomers

Table S5. Characterization of the fresh and spent AL-Py-500 catalyst.

Cycle number	Total acid amount (mmol/g) ^a	Density of each acid functional group			
		Sulfonic groups	Carboxylic groups	Lactonic groups	Phenolic and thiol groups
		(mmol/g) ^b	(mmol/g) ^c	(mmol/g) ^a	(mmol/g) ^a
Fresh ¹	0.11	0.06	0.04	0.00	0.01
1 st	0.09	0.04	0.04	0.00	0.01
2 nd	0.08	0.03	0.04	0.00	0.01
3 rd	0.06	0.03	0.03	0.00	0.00

^aBoehm titration method with 0.01 M NaOH, 0.01 M NaHCO₃, and 0.01 M Na₂CO₃;

^bestimated by acid-base back titration of 0.1 M NaCl method; ^cestimated by the difference of Boehm titration method with 0.01 M NaHCO₃ and acid-base back titration of 0.1 M NaCl method.

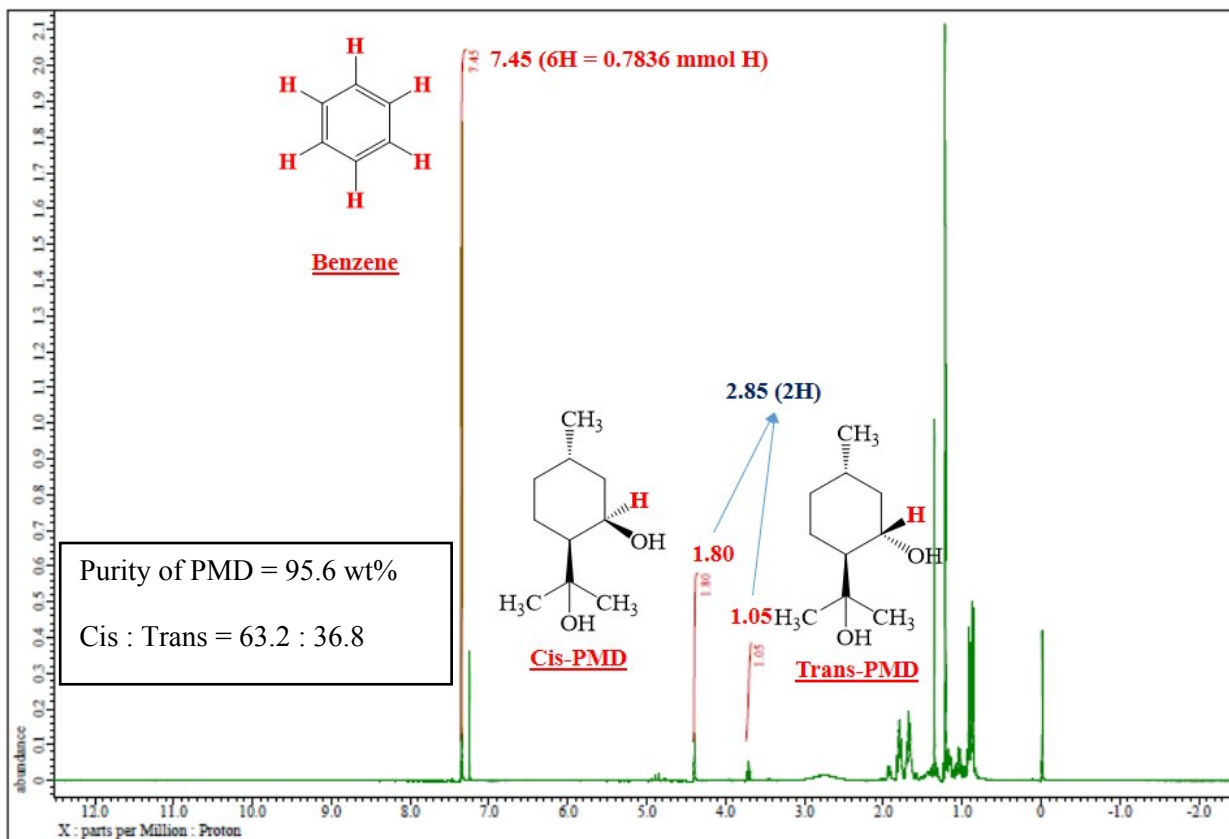
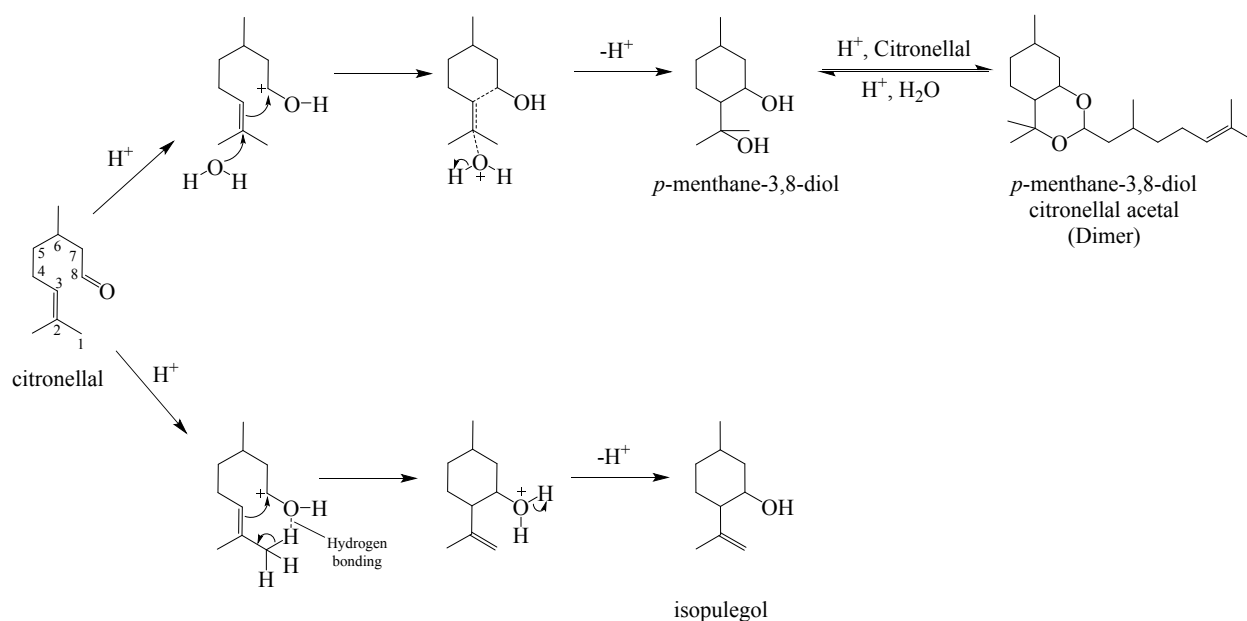


Figure S1. Characterization of standard PMD by $^1\text{H-NMR}$ ($W_{\text{benzene}} = 10.2 \text{ mg}$; $W_{\text{sample}} = 54 \text{ mg}$)

The preparation of standard PMD was followed the reported method.² Herein, (-) citronellal was used as the reactant. The cyclization-hydration of citronellal was conducted with the 7 wt% citric acid solution to (-)-citronellal ratio of 1.5 at 50 °C for 15 h. $^1\text{H-NMR}$ spectrum was compared with the database from Spectral Database for Organic Compounds (SDBS) website, in which Cis-PMD and Trans-PMD are $^1\text{H-NMR}$ SDBS No. 19406HSP-47-008³ and $^1\text{H-NMR}$ SDBS No. 19407HSP-47-007,⁴ respectively. The purity of *p*-menthane-3,8-diol was calculated as follows:

$$\text{Purity of PMD (wt.\%)} = \frac{W_{\text{benzene}} \times \text{Total intensity of specific proton of PMD} \times Mr_{\text{PMD}}}{Mr_{\text{benzene}} \times \text{Total proton of benzene} \times W_{\text{sample}}}$$



Scheme S1. Proposed reaction mechanism in the cyclization-hydration of citronellal to PMD.

Isopulegol is formed by the concerted reaction of ring-closure and deprotonation from the methyl group on the C1 position, in which the intra-molecular hydrogen bonding between the carbonyl oxygen atom and the hydrogen atom connecting to the carbon atom on the C1 position directs this reaction (Scheme S1). Based on this reported assumption, weaker acidity or fewer acid amount is not enough to polarize the carbonyl oxygen atom to form this intra-molecular hydrogen bonding, and instead the positively charged carbon atom on the C2 position during the ring-closure was attacked by water molecule to form PMD. In this proposed reaction pathway, the intermediates toward the isopulegol and PMD formation are different. Actually, when isopulegol was used as a reactant instead of citronellal, none of PMD was formed in the presence of the AL-Py-500 catalyst as well as 7 wt% of citric acid and 0.25 wt% of sulfonic acid, indicating that isopulegol is not an intermediate product for PMD formation in the current reaction conditions (Table S2, entries 2-4).

References

- 1 I. Kurnia, A. Yoshida, N. Chaihad, A. Bayu, Y. Kasai, A. Abudula and G. Guan, *Fuel Process. Technol.*, 2019, **196**, 106175.
- 2 J. Drapeau, M. Rossano, D. Touraud, U. Obermayr, M. Geier, A. Rose and W. Kunz, *Comptes Rendus Chim.*, 2011, **14**, 629–635.
- 3 (1alpha,3beta,4beta)-*p*-menthane-3,8-diol, <https://sdfs.db.aist.go.jp>, (accessed 18 December 2019).
- 4 (1alpha,3alpha,4beta)-*p*-menthane-3,8-diol, <https://sdfs.db.aist.go.jp>, (accessed 18 December 2019).