

Supporting Information

An efficient and greener process for the production
of *p*-menthane-3,8-diols using biosourced
ammonium salts as catalysts.

Andrii Stanovych,^a Franck Pelissier,^a Claire M. Grison,^a Claude Grison^{a}*

^a Laboratory of Bio-inspired Chemistry and Ecological (ChimEco), UMR 5021, National
Centre for Scientific Research – University of Montpellier, 34790 Grabels, France.

* corresponding author: claude.grison@cnrs.fr

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I. ANALYSIS – QUANTIFICATION

Table S 1: Parameters of each compound quantified by GC-MS

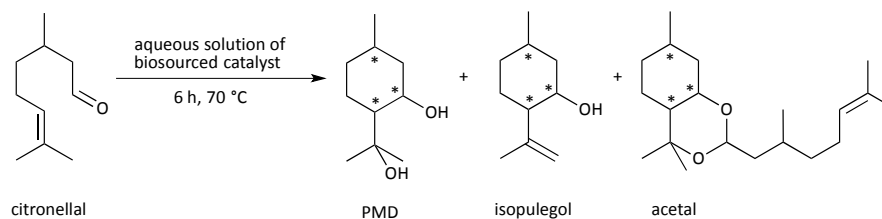
compound	nb	m/z	curve	calibration curve	r ²	LOD	LOQ	C _{max}
Linalool	1	93.05	linear	$Y = 7.23986e+007 * X$	0.9863	0.0005	0.002	0.019
Citronellal	2	95.05	quadratic	$Y = 2.64151e+007 * X + 4.5135e+007 * X^2$	0.9917	0.005	0.036	0.324
Isopulegol	3	121.07	quadratic	$Y = 2.67607e+007 * X + 3.67638e+007 * X^2$	0.9912	0.005	0.04	0.640
Citronellol	4	81.03	quadratic	$Y = 6.46504e+007 * X + 8.24682e+007 * X^2$	0.9939	0.005	0.04	0.320
Geraniol	5	93.04	linear	$Y = 1.47686e+008 * X$	0.9966	0.005	0.04	0.327
<i>cis</i> -PMD1	6 ₁	81.03	quadratic	$Y = 9.09717e+007 * X + 1.68812e+008 * X^2$	0.9891	0.005	0.036	0.290
<i>cis</i> -PMD2	6 ₂	81.03						
<i>trans</i> -PMD3	6 ₃	81.03						
<i>trans</i> -PMD4	6 ₄	81.03						
Acetal1	7 ₁	137.12	quadratic	$Y = 7.97292e+007 * X + 5.01158e+008 * X^2$	0.9869	0.02	0.02	0.162
Acetal2	7 ₂	137.12						

1) Synthesis

a) Synthesis of PMD from citronellal

i. quantification of PMD and side products

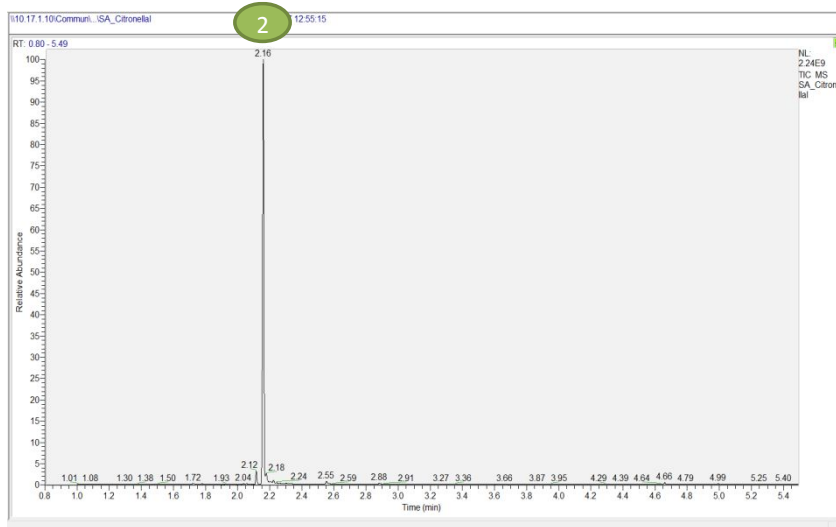
Table S 2: Quantification of compounds for the synthesis of PMD from citronellal



Catalyst	Catalytic loading (% wt)	Conv. (%)	Select. (%)	citronellal (%)	PMD (%)	isopulegols (%)	acetals (%)	degradation (%)
Citric acid	0.2	84	91	16	77	5	2	0
H ₃ N-His-OMe,Cl	0.4	46	99	54	45	1	0	0
	1	100	93	0	93	5	2	0
H ₃ N-Gly-OMe,Cl	0.4	51	100	49	51	0	0	0
	1	96	94	4	90	5	1	0
Vit B1,Cl•HCl	0.4	91	94	9	85	5	1	0
	1	91	93	9	86	4	1	0
Me ₃ N-Gly-OH,Cl	0.2	100	90	0	90	7	3	0
	0.05	83	95	17	79	3	1	0
HCl	0.2	90	71	10	64	10	7	6

ii. GC-MS traces

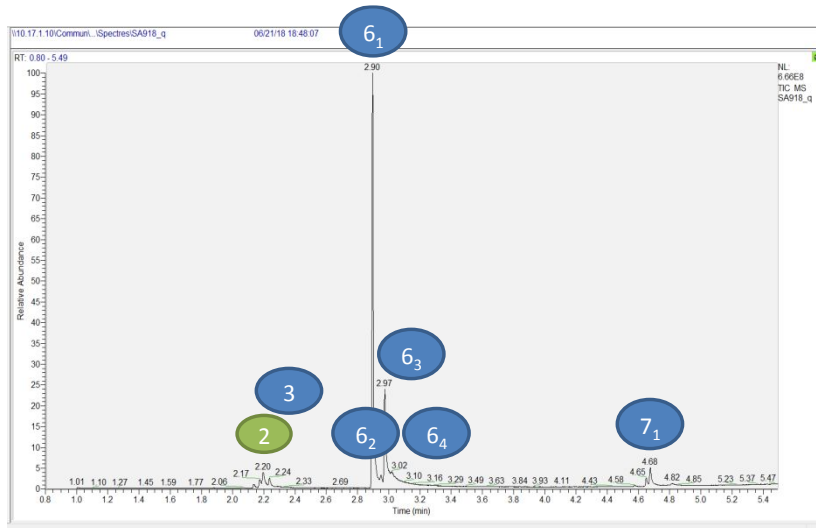
Figure S 1. GC-MS trace of citronellal



List of compounds

- 2 citronellal
- 3 isopulegol
- 6₁ *cis*-PMD1
- 6₂ *cis*-PMD2
- 6₃ *trans*-PMD3
- 6₄ *trans*-PMD4
- 7₁ acetal1

Figure S 2. GC-MS trace of citronellal + betain hydrochloride (0.2%) after 6 h, at 70 °C.



- 2 citronellal
- 3 isopulegol
- 6₁ *cis*-PMD1
- 6₂ *cis*-PMD2
- 6₃ *trans*-PMD3
- 6₄ *trans*-PMD4
- 7₁ acetal1

b) Recycling of catalyst

Table S 3: Quantification of compounds for the recycling of betain hydrochloride solution

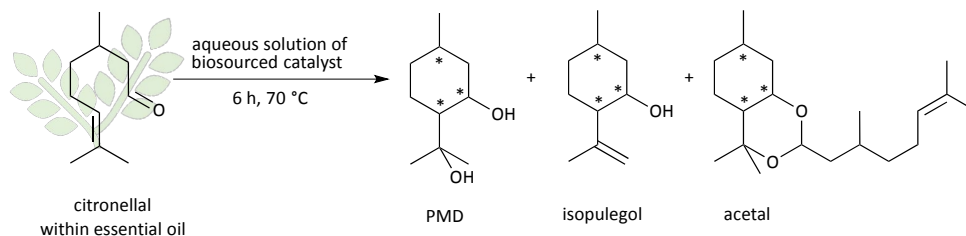
citronellal $\xrightarrow[6\text{ h, } 70\text{ }^\circ\text{C}]{\text{betain hydrochloride (0.2\%)}}$ PMD + isopulegol + acetal

Run	Conv. (%)	Select. (%)	citronellal (%)	PMD (%)	isopulegols (%)	acetals (%)
1	100	90	0	90	6	4
2	98	92	2	90	4	4
3	95	92	5	87	4	4
4	97	91	3	89	4	4
5	98	91	2	89	4	4
6	98	91	2	90	4	4
7	97	91	3	89	4	4

c) Synthesis of PMD from EO

i. quantification of PMD and side products

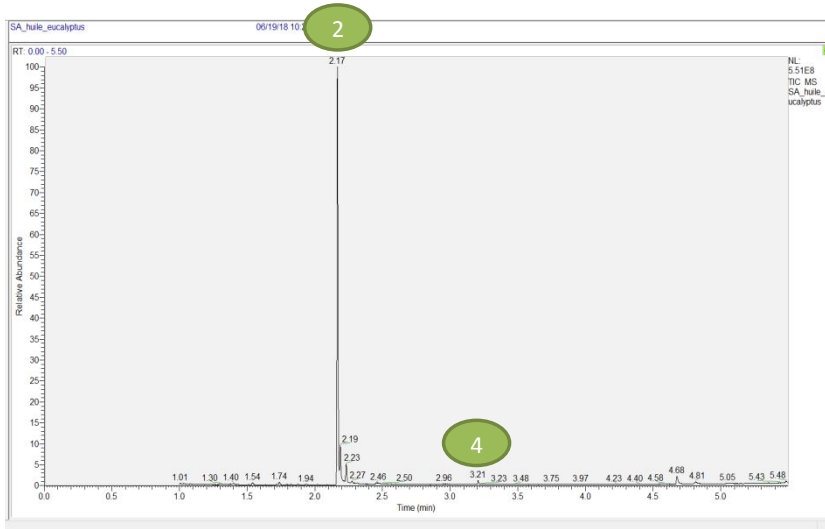
Table S 4: Quantification of compounds for the synthesis of PMD from EO rich in citronellal



Essential Oil	Catalyst	Conv. (%)	Select. (%)	citronellal (%)	PMD (%)	isopulegol (%)	acetal (%)	citronellol (%)	linalool (%)	geraniol (%)
<i>Eucalyptus citriodora</i>	citric acid	86	90	2	85	8	2	3	0	0
	H ₃ N-His-OMe,Cl	99	85	1	82	12	3	3	0	0
	H ₃ N-Gly-OMe,Cl	90	83	10	72	12	3	3	0	0
	Vit B1,Cl•HCl	92	84	8	74	13	2	3	0	0
	Me ₃ N-Gly-OH,Cl	98	87	2	82	7	5	4	0	0
<i>Cymbopogon winterianus</i>	H ₃ N-His-OMe,Cl	98	92	1	48	4	0	15	3	29
	H ₃ N-Gly-OMe,Cl	92	92	4	45	4	0	15	2	30
	Vit B1,Cl•HCl	73	91	15	36	3	0	14	1	30
	Me ₃ N-Gly-OH,Cl	93	96	4	45	2	0	14	2	34
<i>Citrus hystrix</i>	H ₃ N-His-OMe,Cl	92	91	7	77	7	1	5	3	0
	H ₃ N-Gly-OMe,Cl	89	91	10	74	7	1	5	3	0
	Vit B1,Cl•HCl	65	90	32	53	5	0	5	3	0
	Me ₃ N-Gly-OH,Cl	89	93	11	93	4	1	5	3	0

ii. GC-MS traces

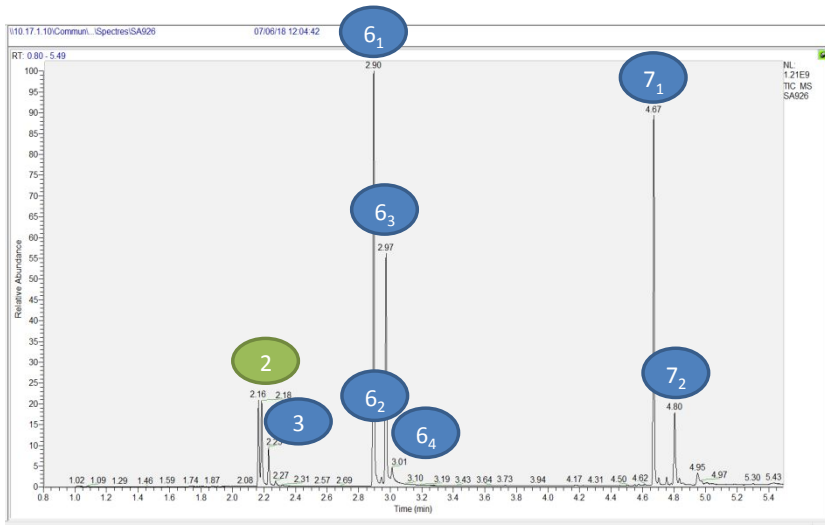
Figure S 3. GC-MS trace of essential oil of *Eucalyptus citriodora*.



List of compounds

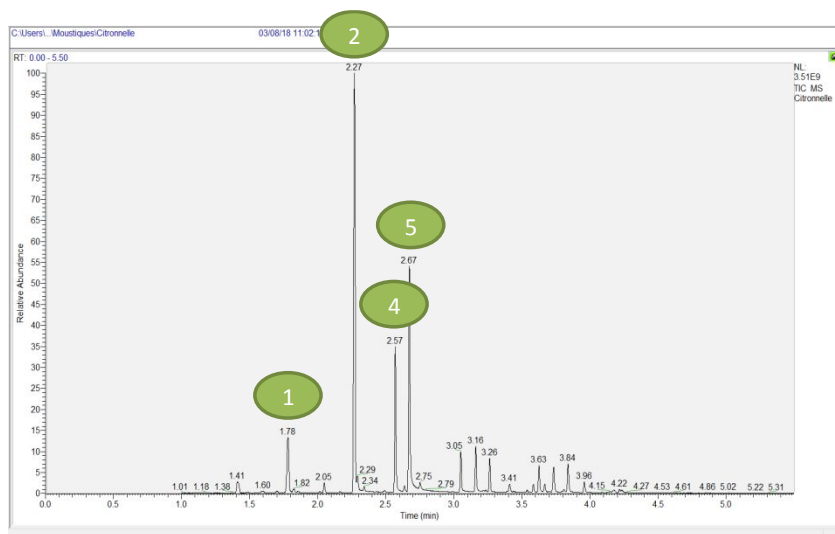
- 1 linalool
- 2 citronellal
- 3 isopulegol
- 4 citronellol
- 5 geraniol
- 6₁ cis-PMD1
- 6₂ cis-PMD2
- 6₃ trans-PMD3
- 6₄ trans-PMD4
- 7₁ acetal1
- 7₂ acetal2

Figure S 4. GC-MS trace of essential oil of *Eucalyptus citriodora* + betain hydrochloride (0.2%) after 6 h, at 70 °C.



- 1 linalool
- 2 citronellal
- 3 isopulegol
- 4 citronellol
- 5 geraniol
- 6₁ cis-PMD1
- 6₂ cis-PMD2
- 6₃ trans-PMD3
- 6₄ trans-PMD4
- 7₁ acetal1
- 7₂ acetal2

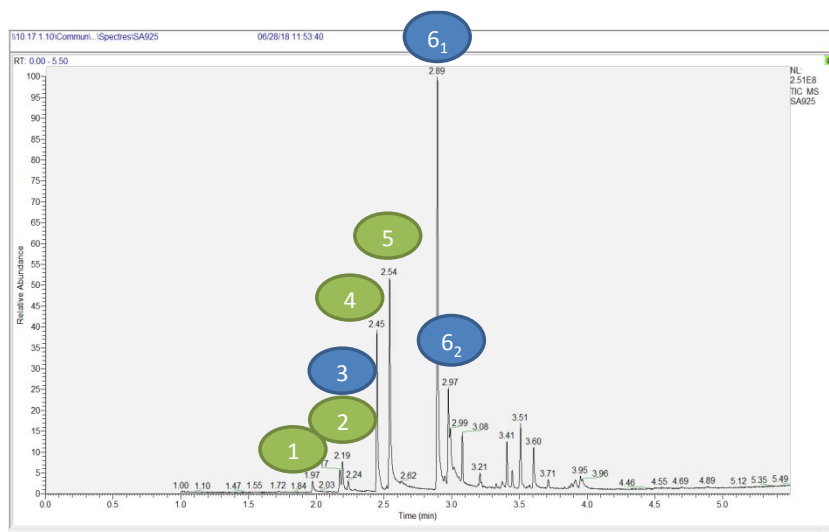
Figure S 5. GC-MS trace of essential oil of *Cymbopogon winterianus*.



List of compounds

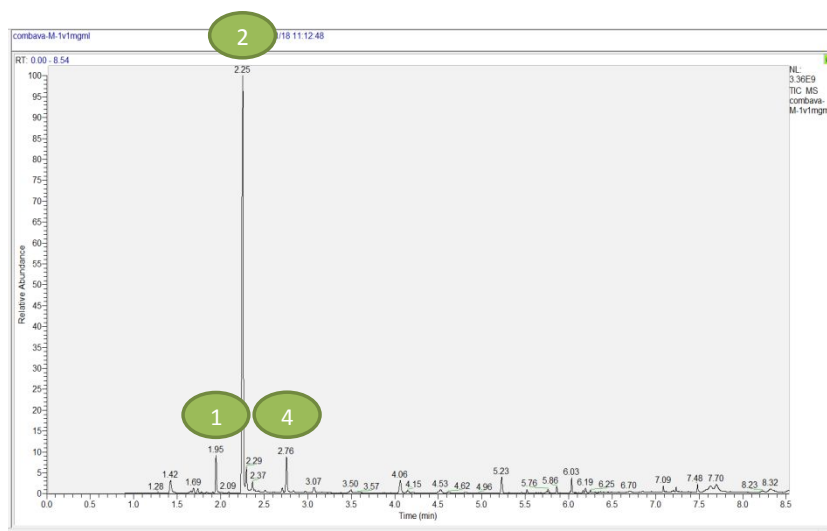
- 1 linalool
- 2 citronellal
- 3 isopulegol
- 4 citronellol
- 5 geraniol
- 6₁ cis-PMD1
- 6₂ cis-PMD2
- 6₃ trans-PMD3
- 6₄ trans-PMD4
- 7₁ acetal1
- 7₂ acetal2

Figure S 6. GC-MS trace of essential oil of *Cymbopogon winterianus* + betain hydrochloride (0.2%) after 6 h, at 70 °C.



- 1 linalool
- 2 citronellal
- 3 isopulegol
- 4 citronellol
- 5 geraniol
- 6₁ cis-PMD1
- 6₂ cis-PMD2
- 6₃ trans-PMD3
- 6₄ trans-PMD4
- 7₁ acetal1
- 7₂ acetal2

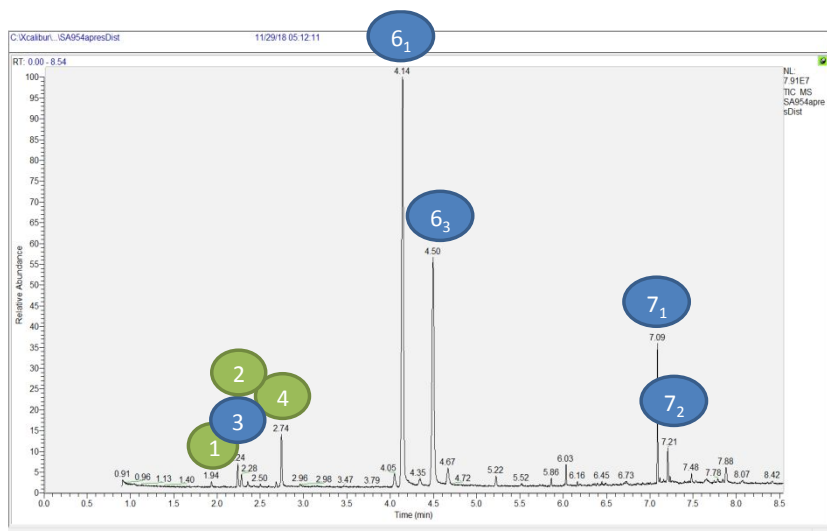
Figure S 7. GC-MS trace of essential oil of *Citrus hydrix*.



List of compounds

- 1 linalool
- 2 citronellal
- 3 isopulegol
- 4 citronellol
- 5 geraniol
- 6₁ cis-PMD1
- 6₂ cis-PMD2
- 6₃ trans-PMD3
- 6₄ trans-PMD4
- 7₁ acetal1
- 7₂ acetal2

Figure S 8. GC-MS trace of essential oil of *Citrus hydrix* + betain hydrochloride (0.2%) after 6 h, at 70 °C.



- 1 linalool
- 2 citronellal
- 3 isopulegol
- 4 citronellol
- 5 geraniol
- 6₁ cis-PMD1
- 6₂ cis-PMD2
- 6₃ trans-PMD3
- 6₄ trans-PMD4
- 7₁ acetal1
- 7₂ acetal2

II. METHOD OF CALCULATION OF GREEN METRICS

Optimum Efficiency (OE)

$$\text{OE (\%)} = \frac{\text{Reaction Mass Efficiency}}{\text{Atom Efficiency}} \times 100 = \frac{\frac{\text{mass of isolated final product}}{\text{total mass of reactants}}}{\frac{\text{molecular weight of final product}}{\text{molecular weights of all reactants}}} \times 100$$

Process Mass Intensity (PMI)

$$\text{PMI} = \frac{\text{total mass of reactants}}{\text{mass of final product}}$$

Turn-Over Number (TON)

$$\text{TON} = \frac{\text{total moles of limiting reactants of all runs}}{\text{moles of catalysts used for all runs}} \times \text{mean of all yields}$$

Turn-Over Frequency (TOF)

$$\text{TOF (h}^{-1}\text{)} = \frac{\text{TON}}{\text{reaction time of all catalysed reactions}}$$

E-factor

$$E_{\text{factor}} = \frac{\text{total mass of all wastes (for all runs, reaction and workup)}}{\text{total mass of final product (for all runs)}}$$

Energy

$$E \text{ (h.}^\circ\text{C)} = (\text{reaction time}) \times (\text{reaction temperature})$$

Since data of electric power are not available for each electric equipment used to perform a chemical reaction followed by its workup in literature, the calculation of energy could not be done in Joules and was simplified.