Supplementary information

Synthesis of methyl propanoate by Baeyer-Villiger monooxygenases

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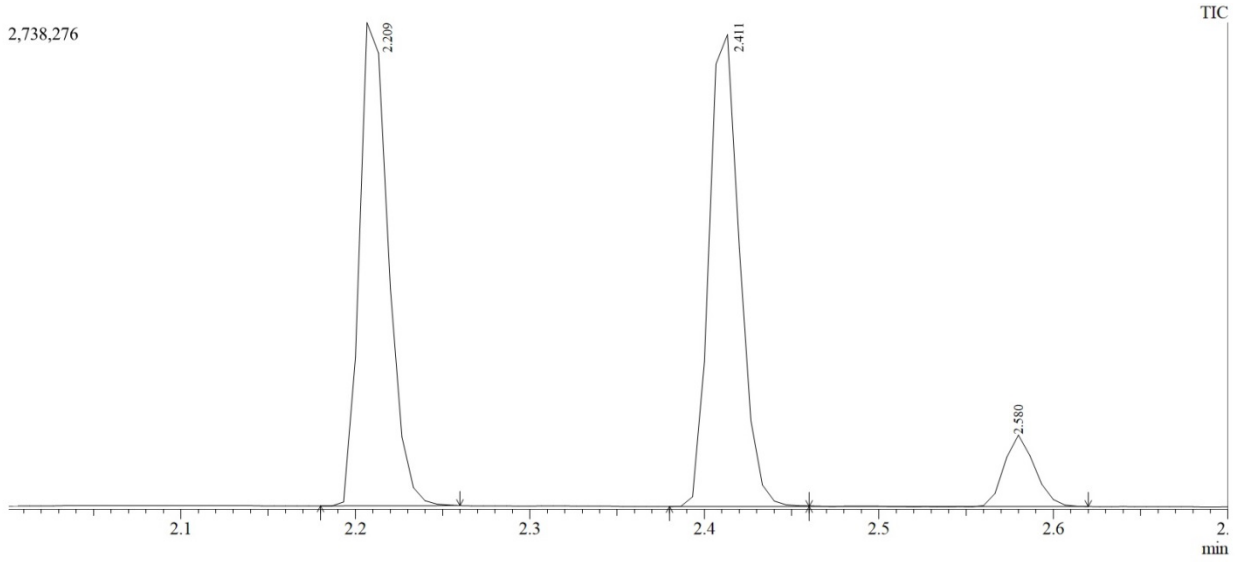
Experimental

All chemicals were purchased from Sigma-Aldrich, ABCR, Biosynth, Oriental Yeast Co. or Merck and used without further purification.

Biocatalysis using growing cells was performed by inoculating 1 mL of LB_{amp} with 50 µL preculture in a 20 mL glass headspace vial fitted with a metal cap and a silicone/PTFE septum, growing the cells at room temperature for 2 h, subsequently expression was induced by the addition of 0.02 % (w/v) L-arabinose and the reaction initiated by adding 10 mM **1**. After 24 h at the optimal temperature for expression (17 – 37 °C), the samples were analysed by headspace GC.

PTDH-$CHMO_{Ac}$ was purified as described previously[1]. For the biocatalysis experiments using isolated enzyme, 4 µM PTDH-CHMO, increasing concentrations of **1**, 20 mM Na_2HPO_3, 100 µM NADPH and 10 µM FAD in 1 mL 50 mM Tris-HCl pH 8.5 were incubated for 24 h at room temperature in a 20 mL headspace vial.

GC analyses were carried out on a Shimadzu GC-QP2010 gas chromatograph with a MS detector using a HP1 column. 250 µl samples were taken from a 20 mL headspace vial with a 45 °C syringe after vials were heated to 40 °C for 2:30. The injection temperature was 150 °C and the oven temperature was set at 35 °C (isothermal). Retention times of the compounds were 2.21 min for **1**, 2.41 min for **2** and 2.58 min for **3**. The compounds were accurately identified by MS and the retention times were consistent compared to the commercially available reference compounds. Peak areas were converted to concentrations using reference samples with known concentrations. Conversions were calculated as the fraction of **1** and **2** of the total amount of **1**, **2** and **3** present after the reaction time.



Peak Report TIC

Peak#	R.Time	I.Time	F.Time	Area	Area%	Height	Height%	A/H	Mark	Name
1	2.209	2.180	2.260	3150172	45.75	2718207	47.05	1.15		2-Butanone
2	2.411	2.380	2.460	3247358	47.16	2656317	45.98	1.22		Ethyl Acetate
3	2.580	2.460	2.620	488562	7.09	402321	6.96	1.21	V	Methyl propionate
				6886092	100.00	5776845	100.00			

Figure 1. Sample chromatogram.