

Titre : Nouvelles Oxidoreductases fongiques pour la synthèse sélective des dérivés oxydés du 5-hydroxyméthylfurfural dont l'acide 2,5-furandicarboxylique

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Principaux résultats: 5-Hydroxyméthylfurfural (HMF), a major residual component of a lignocellulosic bio-refinery process, can be transformed into fundamental building blocks for green chemistry via oxidation. While chemical methods are well established, interest is also being directed into the enzymatic oxidation of HMF into the bio-plastic precursor 2,5-furandicarboxylic acid (FDCA). We demonstrate that three glyoxal oxidases (*PciGLOX*) isoenzymes from the Basidiomycete fungus *Pycnoporus cinnabarinus* were able to oxidize HMF, with *PciGLOX2* and *PciGLOX3* being the most efficient. The major reaction product obtained with the three isoenzymes was 5-hydroxyméthyl-2-furancarboxylique (HMFCFA), a precursor in polyesters and pharmaceuticals production, and very little subsequent conversion of this compound was observed. However, small concentrations of FDCA, a substitute for terephthalic acid in the production of polyesters, were also obtained. The oxidation of HMF was significantly boosted in the presence of catalase for *PciGLOX2*, leading to 70% HMFCFA yield. The highest conversion percentages were observed on 2,5-furandicarboxaldehyde (DFF), a minor product from the reaction of *PciGLOX* on HMF. To bypass HMFCFA accumulation and exploit the efficiency of *PciGLOX* in oxidizing DFF and 5-formyl-2-furan carboxylique (FFCA) towards FDCA production, HMF was oxidized in a cascade reaction with an aryl alcohol oxidase (*UmaAAO*). After 2 h of reaction, *UmaAAO* completely oxidized HMF to DFF and further to FFCA, with FDCA only being detected when *PciGLOX3* was added to the reaction. The maximum yield of 16% FDCA was obtained 24 h after the addition of *PciGLOX3* in the presence of catalase. At least two conversion pathways for HMF oxidation can be considered for *PciGLOX*; however, the highest selectivity was seen towards the production of the valuable polyester precursor HMFCFA. The three isoenzymes showed differences in their catalytic efficiencies and substrate specificities when reacted with HMF derivatives.

Publications:

[1] Daou Marianne, Bassem Yassine, Saowanee Wikee, Eric Record, Françoise Duprat, Emmanuel Bertrand and Craig B. Faulds (2019). « *Pycnoporus Cinnabarinus* Glyoxal Oxidases Display Differential Catalytic Efficiencies on 5-Hydroxyméthylfurfural and Its Oxidized Derivatives ». *Fungal Biology and Biotechnology* 6, no 1

Congrès:

[1] Daou Marianne.; Saowanee Wikee, François Piumi, Daniel Cullen, Emmanuel Bertrand; Marie-Noëlle Rosso, Eric Record, Craig B Faulds (2017) Glyoxal oxidases from *Pycnoporus cinnabarinus* for Green Chemistry Applications, International Symposium on Green Chemistry, May16-19th 2017, La Rochelle, France

Suite donnée au projet : Une suite à ce projet a été déposée et acceptée à l'Institut Carnot 3BCAR (Bioénergies, Biomolécules et matériaux Biosourcés du Carbone Renouvelable) et a permis de financer deux postdoctorants pour une durée de 24 mois au total.