EXPLORING MARINE CARBOHYDRATES: P450-CATALYZED DEMETHYLATION AND IDENTIFICATION OF A COMPLETE "PUL" FOR POLYSACCHARIDE DEGRADATION

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Marine carbohydrates present in algal biomass are an emerging sustainable raw material for bioeconomy. The exploitation of algae as carbon source is hampered by our rather limited knowledge about the microbial pathways present in marine bacteria that can convert algal polysaccharides into oligo- and monosaccharides for fermentation into bioethanol or other compounds.

We have recently shown a distinct metabolic function of P450-monooxygenases in the degradation of agarose or porphyran, where the P450 enzymes (originating from *Formosa agariphila* or *Zobiella galactinovorans*) together with appropriate redox partners catalyze the demethylation of 6-*O*-methyl-D-galactose [1]. Furthermore, we have determined the crystal structure of the P450 enzyme and identified key residues essential for catalysis and substrate recognition [2].

More recently, we could elucidate the entire metabolic pathway involved in the degradation of a major cell wall polysaccharide using a set of enzymes present in the marine flavobacterium *Formosa agariphila* in a distinct and so far unexplored polysaccharide utilization locus (PUL). The pathway consists of 12 carbohydrate-active enzymes, including lyases, sulfatases and glycoside hydrolases that sequentially break down the complex polysaccharide into fermentable monosaccharides. For all previously unknown enzymes we performed a detailed biochemical characterization, determined several crystal structures and could identify the structures of all oligosaccharide intermediates formed during the complex enzymatic degradation by NMR spectroscopy and MS analysis [3].

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