116. Structural studies of β-aryl ether lignin degradation

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Project Goals: To use biochemical and structural methods to characterize the lignin β-aryl ether degradation pathway from Sphingobium sp. SYK-6. The information gained can be applied to enhance the degradation of lignin in the processing of second-generation biofuels and to develop valuable aromatics and other renewable chemicals from lignin streams.

Lignin is both a major obstacle to the sugar release from lignocellulosic biomass for the production of second-generation biofuels and a potential source of aromatics and other valuable chemicals. Degradation of lignin has been relatively well characterized in fungi, and is becoming better understood in bacteria. A catabolic pathway for the enzymatic cleavage of β-aryl ether linkages, which account for 50–70 % of all inter-unit linkages in lignin, has been previously identified in the bacterium Sphingobium sp. SYK-6. Here we present a structural characterization of the two β-etherase enzymes in this degradation pathway, the glutathione S-transferase (GST) enzymes LigE and LigF. LigE and LigF catalyze the regiospecific, glutathione-dependent cleavage of the β-ether bond in (βR)- or (βS)-(3'-methoxyphenoxy)-γ-hydroxypropiovanillone (MPHPV) to release guaiacol and (βS)- or (βR)- glutathionyl adduct of γ-hydroxypropiovanillone, respectively. Although both structures follow the canonical GST fold architecture, an N-terminal thioredoxin- like binding domain and a C-terminal all α-helical domain, each forms a unique dimer interface resulting in distinctly different substrate binding pockets on opposite sides of the active site channel. Understanding the mechanism of β-aryl ether cleavage has great potential for the effective breakdown of lignin in biofuels processing. This new information can enhance our ability to efficiently degrade lignin and to enhance its use as a source of valuable aromatics and other renewable aromatic chemicals.

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