Structural Biology of Ligninolytic Enzymes: Laccases and Heme Peroxidases

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Laccases (Lac) and certain peroxidases, e.g. lignin peroxidase (LiP), manganese peroxidase (MnP), and versatile peroxidase (VP) are employed by filamentous fungi to degrade the recalcitrant bio-polymer lignin a major constituent of woody plants. While LiP, MnP, and VP are heme-containing glycoproteins utilizing hydrogen peroxide as co-substrate to attain the redox state needed for activity, laccase is a blue multi-copper oxidase using molecular oxygen for activation. These fungal metalloenzymes are used in biotechnological applications and have a high potential to be employed in other industrial processes. We have been engaged in structural-functional work on LiP/MnP and VP since many years. This work resulted in the finding of a unique, unprecedented amino acid modification in LiP, which initiated further investigations employing crystallography, protein chemistry, site-directed mutagenesis, spectroscopy, and spin-trapping. The conclusions drawn from the outcome of these experiments had far reaching consequences for the understanding on LiP substrate interaction and on the redox behavior. More recently, we have extended our interest towards fungal laccases, yielding the first crystal structure of a laccase in its glycosylated, fully functional form, containing a full complement set of coppers. In this presentation the current state on structural-functional aspects of the above metallo-enzymes is reviewed, spanning from the description and analysis of 3D-structures to mechanistic aspects, e.g. substrate binding and specificity and redox potential.

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