Lignin-Degrading Enzyme from Phanerochaete chrysosporium

T. K. KIRK AND M. TIEN

Forest Products Laboratory, Madison, Wisconsin, USA

ABSTRACT

The extracellular fluid of ligninolytic cultures of the white-rot wooddestroying fungus, Phanerochaete chrysosporium Burds., contains an enzyme that degrades lignin model compounds as well as lignin itself (1). Like ligninolytic activity, the enzyme appears during idiophasic metabolism, which is triggered by nitrogen starvation. The enzyme has been purified to homogeneity by DEAE-Biogel A chromatography, as assessed by SDS polyacrylamide gel electrophoresis, isoelectric focusing, and gel filtration chromatography. These techniques also revealed a molecular weight of 42,000 daltons, and an isoelectric point of 3.4. The purified enzyme exhibits low substrate specificity. It is an oxygenase, but requires hydrogen peroxide for activity. The activity is optimum at 0.15 mM H₂O₂; at concentrations above 0.5 mM, H₂O₂ is inhibitory. Model compound studies have shown that the enzyme catalyzes cleavage between C_{α} and C_{β} in compounds of the type aryl- $C_{\alpha}HOH$ — $C_{B}HR$ - (R = -aryl or -O-aryl), and in the C_{α} -hydroxyl-bearing propyl side chains of lignin. This cleavage produces an aromatic aldehyde moiety from the C_{α} -portion, and a C_{β} -hydroxylated moiety from the C_{β} -portion. Cleavage between C_{α} and C_{β} in arylglycerol- β -aryl ether structures leads indirectly to cleavage of the β-aryl ether linkage, which is the most abundant intermonomer linkage in lignin. The C_β-hydroxyl oxygen comes from molecular oxygen, and not from H₂O₂, as determined by ¹⁸O isotope studies. The pH optimum for these reactions is between 2.5 and 3.0; no activity is observed above pH 5. Formation of the expected aldehydes from spruce and birch lignins, and partial depolymerization of the lignins results from the action of the purified enzyme. In addition to C_{α} — C_{β} cleavage, the enzyme catalyzes aromatic alcohol oxidation, aryl methylene oxidation, hydroxylation at C_{α} and C_{β} in models containing a $C\alpha$ — $C\beta$ double bond, intradiol cleavage in phenylglycol structures, and phenol oxidations.

REFERENCE

1. Tien, M., and Kirk, T. K. (1983), Science 221, 661.