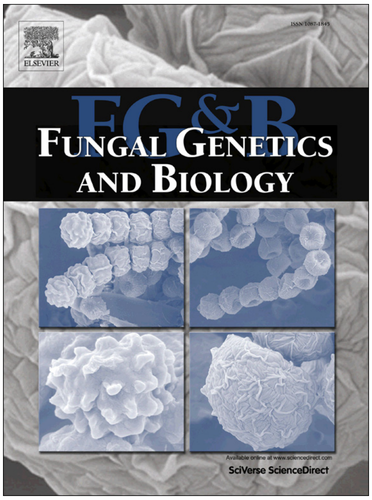

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Copper radical oxidases and related extracellular oxidoreductases of wood-decay Agaricomycetes

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Abstract

Extracellular peroxide generation, a key component of oxidative lignocellulose degradation, has been attributed to various enzymes including the copper radical oxidases. Encoded by a family of structurally related sequences, the genes are widely distributed among wood decay fungi including three recently completed polypore genomes. In all cases, core catalytic residues are conserved, but five subfamilies are recognized. Glyoxal oxidase, the most intensively studied representative, has been shown physiologically connected to lignin peroxidase. Relatively little is known about structure-function relationships among more recently discovered copper radical oxidases. Nevertheless, differences in substrate preferences have been observed in one case and the proteins have been detected in filtrates of various wood-grown cultures. Such diversity may reflect adaptations to host cell wall composition and changing environmental conditions.

1. Introduction

Critical components of the carbon cycle, wood decomposing fungi have received increased attention for their potential in the production of biofuels and other bioprocesses. Most wood-decaying fungi are in the Agaricomycetes (Basidiomycota), although some species also occur in other groups of Basidiomycota and Ascomycota (Gilbertson, 1980; Nilsson et al., 1989; Shary et al., 2007; Wells and Bandoni, 2001). Two broad categories of wood decay chemistries are known in Agaricomycetes; white rot and brown rot. White rot fungi are uniquely capable of efficiently degrading and mineralizing all components of plant cell walls, including the highly recalcitrant lignin fraction. In contrast, brown rot fungi rapidly depolymerize cellulose but do not appreciably remove lignin, which remains as a polymeric residue (Blanchette, 1995; Eriksson et al., 1990; Niemenmaa et al., 2007; Worrall et al., 1997; Yelle et al., 2008). Resistant to further decay, brown rot residues contribute to the carbon pool in humic soils, particularly in conifer-dominated ecosystems. Evidence suggests that white rot is plesiomorphic in Agaricomycetes and that brown rot has evolved repeatedly (Floudas et al., 2012; Hibbett and Donoghue, 2001).

As described below, extracellular peroxide production plays an essential role in white rot and brown rot decay. Copper radical oxidases (CROs), the main focus of this review, likely fulfills this pivotal role.

2. Brown rot mechanisms

White and brown rot wood decay are complex and incompletely understood processes that has been intensively studied in the Polyporales *Phanerochaete chrysosporium* and *Postia placenta*, respectively. Other model white rot fungi include the polypores *Ceriporiopsis subvermispora, Bjerkandera adusta, Trametes versicolor* and the agaric *Pleurotus ostreatus*.