

Synthesis and functional analysis of ceriporic acid, extracellular metabolite of selective white rot fungus *Ceriporiopsis subvermispora*

Hitoe Shimizu

Laboratory of Biomass Conversion, RISH, Kyoto University

Wood is mainly composed of cellulose, hemicelluloses and lignin. Most white rot basidiomycetes simultaneously degrade polysaccharides and lignin. In contrast, a selective white rot fungus *Ceriporiopsis subvermispora* decomposes lignin with minimum damage of cellulose. Important mechanisms for the selective white rot include lignin degradation by low molecular mass agents and inhibition of cellulose degradation by the cellulolytic active oxygen species, hydroxyl radicals ($\cdot\text{OH}$). Previously we reported that production of hydroxyl radicals and cellulose depolymerization were inhibited by ceriporic acid B (1-nonadecene-2,3-dicarboxylic acid), an extracellular metabolite of *C. subvermispora* [1-3]. On the other hand, it was known that this fungus secretes oxalic acid [4], which accelerates hydroxyl radical production at certain molar ratios of oxalate/ Fe^{3+} [5]. In the present study, we analyzed effects of ceriporic acid B on hydroxyl radical production and cellulose degradation by the Fenton reaction system in the presence and absence of oxalic acid.

Hydroxyl radicals were produced by the Fenton system containing Fe^{3+} , H_2O_2 and a reductant in the presence and absence of ceriporic acid B and oxalic acid. Depolymerization of cellulose by the Fenton system was then evaluated by measuring decrease in viscosity of cellulose. In the presence of oxalic acid, hydroxyl radical production and cellulose degradation were accelerated at the equimolar ratio of oxalate and Fe^{3+} . However, addition of ceriporic acid B inhibited the hydroxyl radical production and cellulose degradation at all the molar ratio employed. These results indicate that ceriporic acid B inhibited cellulose degradation, in the presence and absence of oxalic acid.

C. subvermispora secretes (*Z*)-10-nonadecadiene-2,3-dicarboxylic acid (ceriporic acid C), in addition to 1-nonadecene-2,3-dicarboxylic acid (ceriporic acid B) and 1-heptadecene-2,3-dicarboxylic acid (ceriporic acid A) [6,7]. In the present study, (*Z*)-10-nonadecadiene-2,3-dicarboxylic acid (ceriporic acid C) and its (*E*)-isomer was synthesized by the Grignard reaction for structural and functional analysis of the extracellular metabolites.

REFERENCES

- [1] Watanabe, T., Teranishi, H., Honda, Y., Kuwahara, M. (2002) *Biochem. Biophys. Res. Commun.* **297**: 918-923.
- [2] Rahmawati, N., Ohashi, Y., Watanabe, T., Honda, Y., Watanabe, T. (2005) *Biomacromolecules*, **6**: 2851-2856.
- [3] Ohashi, Y., Kan, Y., Watanabe, T., Honda, Y., Watanabe, T. (2007) *Org. Biomol. Chem.*, **5**: 840-847.
- [4] Urzur, U., Kersten, P. J., Vicuña, R. (1998) *Appl. Environ. Microbiol.*, **64**: 68-73.
- [5] Valera, E., and M. Tien, (2003) *Appl. Environ. Microbiol.*, **69**:6025-6031
- [6] Enoki, M., Honda, Y., Kuwahara, M., Watanabe, T. (2002) *Chem. Phys. Lipid*, **120**: 9-20.
- [7] Amirta, R., Fujimori, K., Shirai, N., Honda, Y., Watanabe, T. (2003) *Chem. Phys. Lipids*, **126**: 121-131.