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Evidences that a secondary metabolite is the Fe^{3+}-reductant secreted by an ectomycorrhizal fungus during decomposition of litter material

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Ectomycorrhizal (ECM) fungi are thought to play a key role in mobilizing nutrients embedded in recalcitrant organic matter complexes and thereby making them accessible to the host plant. Recent work combining spectroscopic analyses with transcriptome profiling have indicated the oxidative degradation of litter extract involving Fenton chemistry ($Fe^{2+} + H_2O_2 + H+ \rightarrow Fe^{3+} + \bullet OH + H_2O$) by the ECM fungus *Paxillus involutus*. In many wood-degrading brown-rot fungi, secreted metabolites are one of the component which drive one-electron reductions of Fe^{3+} and O_2, generating Fenton reagents. We therefore investigated if such compounds are also produced by the ECM fungus P. involutus during litter degradation. Activity-guided purification was performed to isolate the Fe^{3+}-reducing compound (s) secreted by *P. involutus* during growth on organic matter extract. The Fe^{3+}-reducing activity correlated with the presence of one compound. Mass spectrometry and NMR identified this compound as the diphenylcyclopentenone pigment involutin. A major part of the involutin produced by the fungus during organic matter decomposition was secreted into the medium and the pigment was not detected when the fungus was grown in a mineral nutrient medium. We also found that under physiological concentration of H_2O_2, involutin has the capacity to drive an in vitro Fenton reaction. Our results suggest that mechanisms for generating the Fenton reagents by secreted metabolites are similar in ECM fungi and saprophytic brown-rot fungi. It remains to be determine whether involutin can reduce Fe^{3+} from mineral complexes in natural soil systems or if cooperative processes including other metabolites are required.