Biomimetic Lignin Cleavage Using Small Thiols

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Project Goals: Depolymerization of lignin and lignin-like structures using small organic thiols that mimic the glutathione in the enzymatic β-aryl ether cleavage pathway.

Lignin valorization for the replacement of petrochemicals is challenging due, in part, to the expensive inputs and/or caustic depolymerization techniques typically required. Lignin-degrading enzymes provide an excellent model for a simple and green cleavage method. In the β-aryl ether cleavage pathway of wood degrading bacteria, the cleavage of β-O-4 bonds occurs in a three-step process: 1) oxidation of the α-carbon hydroxyl group, 2) glutathione nucleophilic attack on the β-carbon, displacing the phenoxide, and 3) reduction of the above-formed glutathione covalent intermediate's S-C bond with a second glutathione, releasing the second lignin fragment and the glutathione disulfide. This work focuses on mimicking this enzymatic pathway using small organic thiols without the aid of proteins or metals. Oxidized lignin dimer models treated with β-mercaptoethanol and related thiols undergo cleavage with yields ranging from 30% to 100% depending on the specific reaction conditions. The sensitivity of this cleavage to lignin-relevant functional groups was probed to determine the scope of the reaction. As in the enzymatic pathway, oxidation of the alpha hydroxy group was found to be necessary. Primary and secondary beta aryl ether bonds were cleaved while tertiary sites were unreactive as expected for S_N2 reactivity. Lastly, the reaction tolerates a variety of functional groups on both the phenolic and keto aromatic rings. Having mechanistically analyzed the reactions in well-defined model dimers, we applied this process to real lignin, achieving approximately 68% molecular weight reduction. This work exemplifies a reductive biomimetic approach to lignin depolymerization by mimicking the nucleophilic thiol-mediated ether cleavage found in the enzymatic β-aryl ether cleavage pathway.

References

1. Hegg, E. L.; Jackson, J. E.; Klinger, G. E. Depolymerizing lignin by reacting lignin compound with thiol compound to depolymerize lignin compound and form depolymerized lignin product having reduced molecular weight relative to lignin compound prior to reacting. U.S. Patent WO2018195000-A1, Oct. 25, 2018.

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