Potential Monolignol Replacements: Synthesis and Lignification of Monolignol γ-Glucosides and β-Hydroxycinnamoyl Glucosides

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ABSTRACT

Bioengineering plants to have more readily hydrolysable lignocellulosics is needed to reap the potential of biomass for liquid biofuel generation. Lignin is a hydrophobic biopolymer and contributes much to the recalcitrance to lignocellulosics toward hydrolysis. We proposed that increasing the hydrophilicity of lignin would increase the energy efficiency of lignocellulose processing. To test this hypothesis, we have synthesized monolignol γ-glucosides and hydroxycinnamoyl glucosides. We have also demonstrated that these compounds are readily incorporated into synthetic lignin, i.e., during in vitro lignification. Our studies have successfully paved the road toward studying the in vitro incorporation of these hydrophilic monolignol surrogates to plant cell walls to explore their influence on lignocellulose hydrolysis.

INTRODUCTION

The long-term goal of our GECP project is to develop a more viable lignocellulosic biomass for liquid biofuel generation. The incorporation of potential monolignol surrogates into lignin, by increasing the complement of the surrogates and taking advantage of the pliability of lignin biosynthesis, will alter the properties of lignin and reduce the barrier of lignocelluloses processing and conversion. The short-term goal of our project is to identify potential monolignol surrogates by means of chemical synthesis and in vitro lignification studies.

STRATEGY

Lignin is a hydrophobic polymer. In plant cell walls, it forms layers over polysaccharides, preventing these biopolymers from hydrolysis. Increasing the hydrophilicity of lignin would alter the wetting property and morphology of lignin and increase the accessibility of polysaccharides for processing and conversion.*

In this poster, we report four hydrophilic monolignols as potential monomer surrogates.** The structures and proposed lignification sites (red arrows) of these monomer surrogates are shown as follows:

1 1-O-β-feruloyl glucoside
2 1-O-β-sinapoyl glucoside
3 1-O-β-coniferyl γ-glucoside
4 1-O-β-sinapoyl γ-glucoside

* Note: we assume that hydrophilic lignins will not be tolerated well in vessel elements, but may be in the xylem fibers; therefore, in planta, the application of xylem-specific promoters is likely to be key.

** Please see the poster of Martina Opieinik et al. from out group for studies on another hydrophilic monolignol.

CONCLUSIONS:

• We have provided efficient synthetic routes to two monolignol γ-glucosides and two β-hydroxycinnamoyl glucosides have been developed. These four hydrophilic monolignol surrogates are readily accessed at the multigram scale.

• Dehydrogenative co-polymerization of these glucosides with coniferyl alcohol produced synthetic lignins in modest to good yields.

• NMR studies established that these hydrophilic monolignol surrogates were incorporated into the synthetic lignins.

• The impact of hydrophilic lignin on biomass processing by cell wall lignification studies is actively under investigation.

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References: