



Biochemical transformation of lignin for deriving valued commodities from lignocellulose

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The biochemical properties of lignin present major obstacles to deriving societally beneficial entities from lignocellulosic biomass, an abundant and renewable feedstock. Similar to other biopolymers such as polysaccharides, polypeptides, and ribonucleic acids, lignin polymers are derived from multiple types of monomeric units. However, lignin's renowned recalcitrance is largely attributable to its racemic nature and the variety of covalent inter-unit linkages through which its aromatic monomers are linked. Indeed, unlike other biopolymers whose monomers are consistently inter-linked by a single type of covalent bond, the monomeric units in lignin are linked via non-enzymatic, combinatorial radical coupling reactions that give rise to a variety of inter-unit covalent bonds in mildly branched racemic polymers. Yet, despite the chemical complexity and stability of lignin, significant strides have been made in recent years to identify routes through which valued commodities can be derived from it. This paper discusses emerging biological and biochemical means through which degradation of lignin to aromatic monomers can lead to the derivation of commercially valuable products.

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Introduction

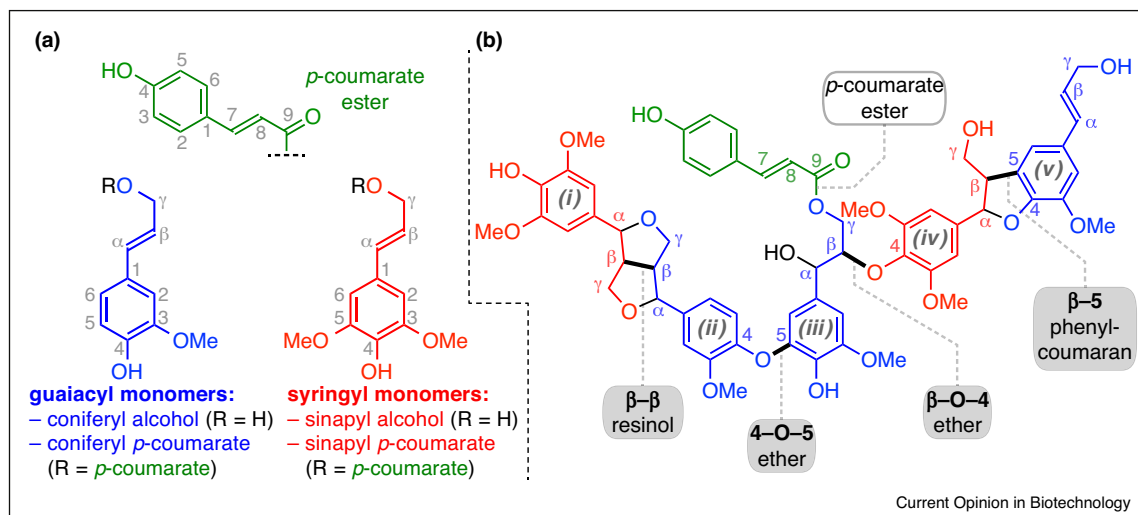
Lignocellulosic biomass is composed of Earth's three most abundant terrestrial biopolymers (cellulose, hemicelluloses, and lignin) and accounts for the majority of

organic carbon in the global budget [1]. Both abundant and renewable, polysaccharides (cellulose and hemicelluloses) are attractive feedstocks for the production of paper, ethanol, and next-generation fuels [2]. Converting lignocellulose to these and other valued commodities is, however, made challenging by the physiochemical constraints placed on polysaccharides by a third biopolymer, lignin. Comprising between 15 and 30% (dry weight) of vascular plant cell walls [3], lignin is a complex and combinatorial polymer derived from a variety of aromatic monomers linked together via heterogeneous chemical bonds, and to which plant polysaccharides may be covalently bound, particularly in grasses [4–6]. Processes designed to simply remove lignin and convert the resulting cellulosic and hemicellulosic components to valued commodities [7,8] often result in the release of aromatic compounds that may be inhibitory to microbial conversion processes [9]. Although the utility of lignin polymers in a variety of industries [10] is attributable to lignin's complexity and stability, these same characteristics create a challenge for its use as a chemical feedstock by biomanufacturers striving to derive low molecular weight products from it. However, there is emerging evidence that bioconversion processes may help convert lignin to useful monomeric products. This paper focuses on recent advances in biotechnology that may enable the derivation of desirable aromatic monomers and certain aliphatic compounds from lignin. It will not address the industrial applications of lignin polymers that have been described elsewhere [10,11,12^{**},13–15].

Lignin's molecular structure

Lignin is crucial to a plant's structural rigidity and plays critical roles in water and nutrient transport [16], as well as conferring resistance to mechanical stress, photodegradation, and various infectious agents [17,18]. The heterogeneous and combinatorial lignin polymers are produced via oxidative coupling of the 'monolignols,' primarily coniferyl alcohol, sinapyl alcohol and, in grasses, their *p*-coumarate esters [6,19,20]. Radical condensation of the monomers, primarily with the growing polymer [21], gives rise to lignin containing guaiacyl and syringyl monoaromatic units that may be sidechain-acylated with *p*-coumarate (Figure 1a) [3,6]. The inherent structural rigidity of lignin is attributable to the non-selective nature with which these monomeric units become covalently cross-linked into the polymer during lignification.

Figure 1



The structural components of lignin in monocots. **(a)** The biosynthetic precursors, coniferyl (blue) and sinapyl (red) alcohols, as well as their cognate *p*-coumarate (green) conjugated esters, coniferyl *p*-coumarate and sinapyl *p*-coumarate, undergo radical coupling to give rise to **(b)** guaiacyl (blue) and syringyl (red) units along with their pendant *p*-coumarates (green) in lignin polymers. A representative oligomer arising from the coupling of sinapyl alcohol (monomers *i* and *iv*), coniferyl alcohol (*ii* and *v*), and coniferyl *p*-coumarate (*iii*) shows the most prominent of the various types of inter-unit covalent linkages in lignin polymers. Ester linkages formed before lignification are labeled (unshaded text). All inter-unit bonds formed during lignification, as well as the hydroxyl groups resulting from post-coupling rearomatization of quinone methide intermediates, are shown in black. The linkages specifically formed by radical coupling reactions are bolded and labeled (shaded text) with the type of unit produced in the polymer.

Lignin biosynthesis is well established to result from the enzymatic radicalization of monolignols and subsequent non-enzymatic coupling of those radicals in the plant apoplast [19,22]. Thus, unlike other biopolymers, lignin's guaiacyl and syringyl monomers are not linked together by a single type of chemical bond. Rather, as monolignol radicals couple with the growing polymer, the bond structure manifested between two monomer units will be characterized by one of several inter-unit linkage types typically found in lignin (Figure 1b): resinols (β - β), 4-O-5 di-aryl ethers, phenylcoumarans (β -5) and, most prominently, β -O-4-aryl ether linkages (termed β -ethers hereafter) [6,23]. Further, because these inter-unit linkages are formed through non-enzymatic coupling of monolignol radicals and the phenolic end-group (radical) of the growing lignin polymer, and because monolignols invariably couple at their β -positions, chiral centers are created at these β -positions with each chain-extending step, and at their α -positions during the subsequent rearomatization [6]. These non-stereoselective coupling reactions therefore result in heterogeneous inter-unit linkage types with variable stereochemical configurations and yield lignin polymers that are racemic and, consequently, more biologically recalcitrant [6,24,25*].

Conversion of lignin polymers to monoaromatic products

Finding industrial applications for lignin polymers has been a decades-long goal, as large amounts of lignin are

produced by the pulp and paper industry. New processes for lignin purification and fractionation have been implemented at an industrial scale [26,27] and applications of purified lignin polymers range from their use as concrete additives to the manufacturing of composite materials in the production of plastics, resins, and textiles [10]. Although these are industrially important applications, the direct use of lignin polymers is not the subject of this paper.

Of emerging interest is the possibility of complete lignin depolymerization to monomers. This is a fascinating research frontier that could lead to the production of valuable aromatic or aliphatic chemicals that are currently produced from fossil fuel resources. Many guaiacyl and syringyl [*i.e.*, compounds bearing a *p*-hydroxy group (*para* to the aliphatic sidechain) and either one or two *meta*-methoxy groups] monoaromatic compounds, such as vanillin and syringaldehyde (Figure 2), are potential lignin derivatives in demand by the biofuel, food, pharmaceutical, and cosmetic industries [28]. Furthermore, this route for lignin valorization is even more promising when biotechnological advances in transgenic plants are taken into account. For example, the recently discovered ability of plants to also utilize monolignol ferulate conjugates as monomers for lignification holds significant promise for incorporating ester bonds into the lignin backbone itself, rendering lignins more amenable to chemical depolymerization [29*] and potentially with improved yields of

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