

Lignin Overview

Wood is composed of many chemical components, primarily extractives, carbohydrates, and lignin, which are distributed nonuniformly as the result of anatomical structure. Lignin is derived from the Latin term *lignum*, which means wood [1]. Anselme Payen (1838) was the first to recognize the composite nature of wood and referred to a carbon-rich substance as the “encrusting material” which embedded cellulose in the wood. Schulze (1865) later defined this encrusting material as lignin. Lignin has been described as a random, three-dimensional network polymer comprised of variously linked phenylpropane units [2]. Lignin is the second most abundant biological material on the planet, exceeded only by cellulose and hemicellulose, and comprises 15-25% of the dry weight of woody plants. This macromolecule plays a vital role in providing mechanical support to bind plant fibers together. Lignin also decreases the permeation of water through the cell walls of the xylem, thereby playing an intricate role in the transport of water and nutrients. Finally, lignin plays an important function in a plant’s natural defense against degradation by impeding penetration of destructive enzymes through the cell wall [1,2]. Although lignin is necessary to trees, it is undesirable in most chemical papermaking fibers and is removed by pulping and bleaching processes.

Biosynthesis

Plant lignins can be broadly divided into three classes: softwood (gymnosperm), hardwood (angiosperm) and grass or annual plant (graminaceous) lignin [3]. Three different phenylpropane units, or monolignols, are responsible for lignin biosynthesis [4]. Guaiacyl lignin is composed principally of coniferyl alcohol units, while guaiacyl-syringyl lignin contains monomeric units from coniferyl and sinapyl alcohol. In general, guaiacyl lignin is found in softwoods while guaiacyl-syringyl lignin is present in hardwoods. Graminaceous lignin is composed mainly of *p*-coumaryl alcohol units. These three lignin precursors are shown in Figure 1. The principles employed in Figure 1 to denote carbon atoms in the side chain will hold throughout this paper.

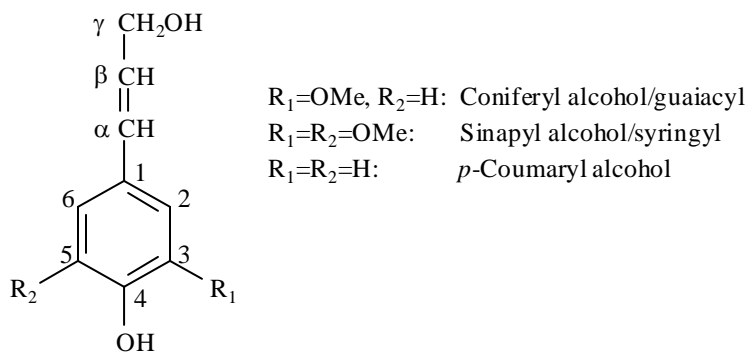
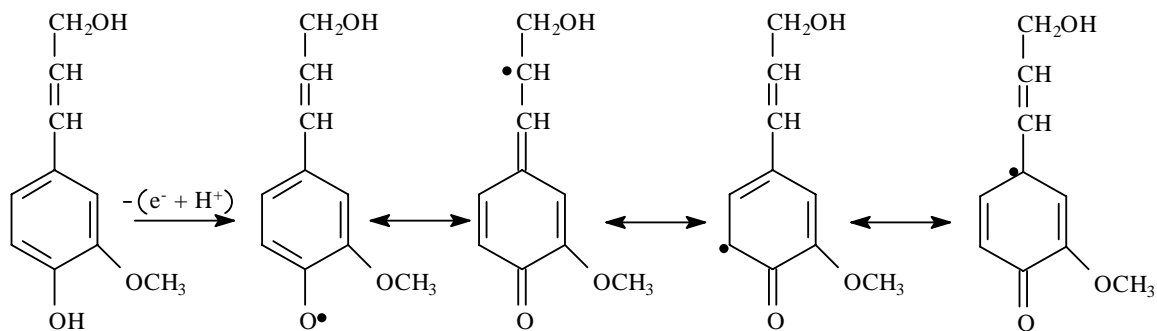


Figure 1. The three building blocks of lignin.

Lignin polymerization is initiated by oxidation of the phenylpropane phenolic hydroxyl groups. Freudenberg has shown that lignin precursors undergo dimerization through enzymatic dehydrogenation, which is initiated by an electron transfer and yields resonance-stabilized phenoxy radicals. Figure 2 shows an example of a phenoxy radical formed from coniferyl alcohol and its resonance forms. Stabilization of the radical occurs by coupling to another radical in any of the positions of the unpaired electron.



Coniferyl alcohol

Figure 2. Formation of resonance-stabilized phenoxy radicals by enzymatic dehydrogenation of coniferyl alcohol.

A monolignol free radical can then undergo radical coupling reactions, producing a variety of dimers, termed dilignols. The combination of monomeric radicals through only β -O-4 and β -5 coupling would lead to a linear polymer. However, branching of the polymer may take place through subsequent nucleophilic attack by water, alcohols or phenolic hydroxyl groups on the benzyl carbon of the quinone methide intermediate. The

dilignols then undergo further endwise polymerization, instead of combining with one another. Figure 3 shows an example of endwise polymerization during lignin biosynthesis.

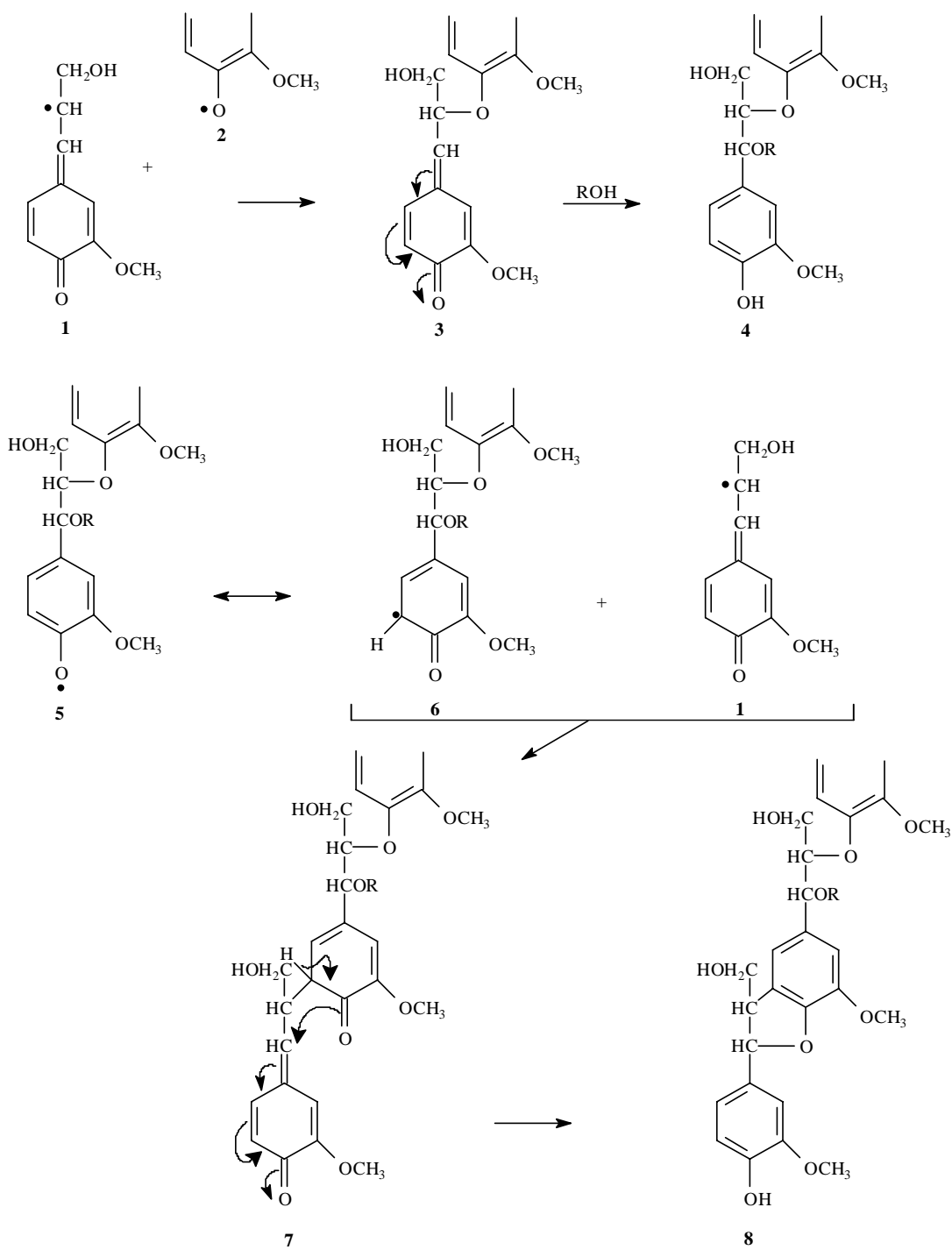


Figure 3. Endwise polymerization during lignin biosynthesis.

Structure

After many years of study, the structure of native lignin still remains unclear. However, the dominant structures in lignin have been elucidated as the methods for identification of the degradation products and for the synthesis of model compounds have improved. The results from these numerous studies have yielded what is believed to be an accurate representation of the structure of lignin. Examples of the elucidated structural features of lignin include the dominant linkages between the phenylpropane units and their abundance, as well as the abundance and frequency of some functional groups. Linkages between the phenylpropane units and the various functional groups on these units give lignin a unique and very complex structure.

Figure 4 shows some of the common linkages found in softwood lignin. The dominant linkage is the β -O-4 linkage. In 1995, Karhunen *et al.* [5, 6] discovered a new 8-membered ring linkage in softwood lignin called dibenzodioxocin. This linkage was found through advanced 2-D NMR techniques and is now proposed to be the main branching point in softwood lignin [7]. The percent abundance of this and other linkages found in softwood lignin has been determined and is shown in

Table 1 [8, 9, 10].

The lignin macromolecule also contains a variety of functional groups that have an impact on its reactivity. Lignin mostly contains methoxyl groups, phenolic hydroxyl groups, and few terminal aldehyde groups. Only a small proportion of the phenolic hydroxyl groups are free since most are occupied in linkages to neighboring phenylpropane linkages. Carbonyl and alcoholic hydroxyl groups are incorporated into the lignin structure during enzymatic dehydrogenation. Table 2 illustrates the frequency of some common functional groups found in lignin.

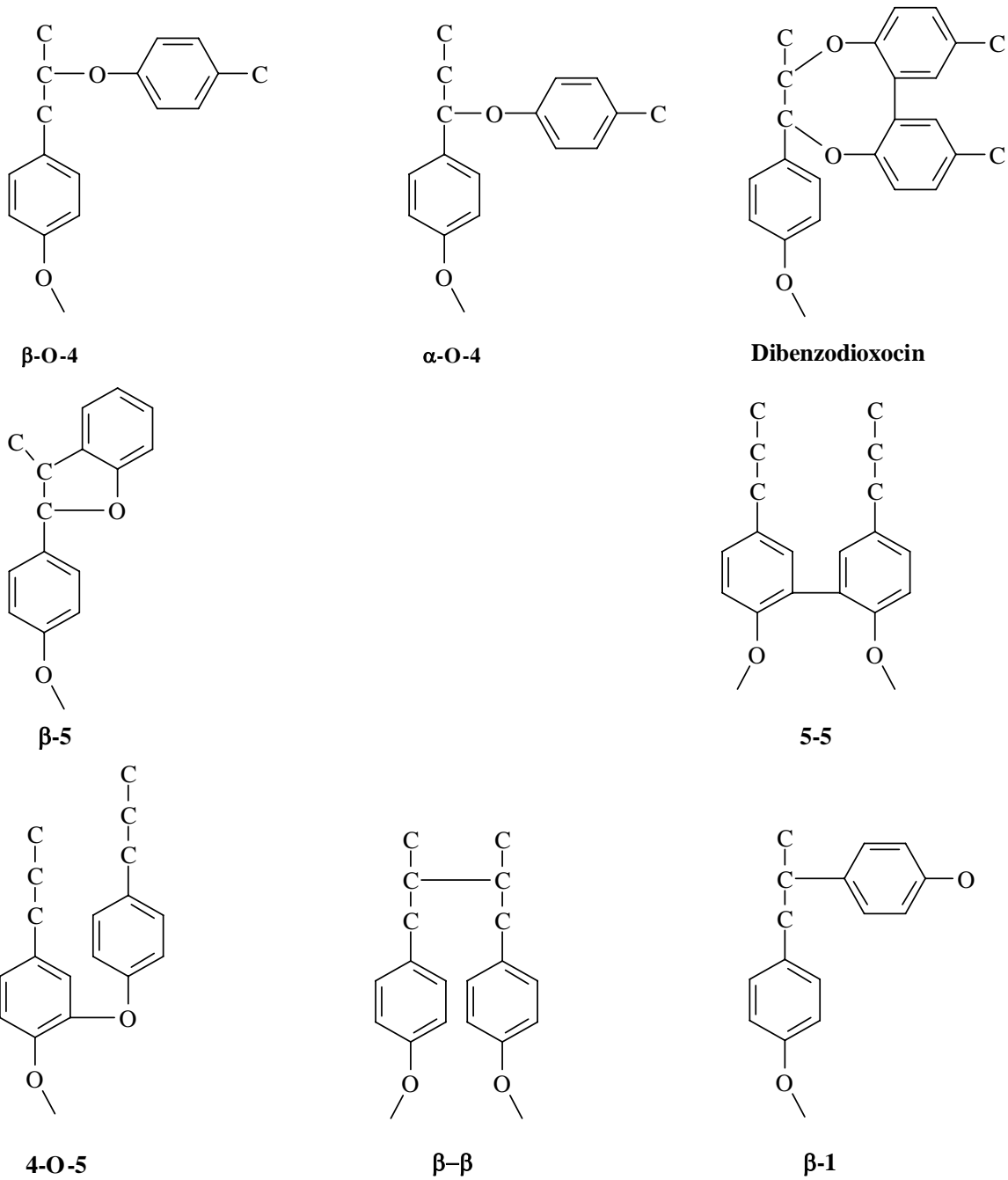


Figure 4. Common phenylpropane linkages in lignin.

Table 1. Linkages found in softwood lignin.

Linkage Type	Dimer Structure	Percent of Total Linkages (%)
β -O-4	Phenylpropane β -aryl ether	45-50
5-5	Biphenyl and Dibenzodioxocin	18-25
β -5	Phenylcoumaran	9-12
β -1	1,2-Diaryl propane	7-10
α -O-4	Phenylpropane α -aryl ether	6-8
4-O-5	Diaryl ether	4-8
β - β	β - β -linked structures	3

Table 2. Functional groups in softwood lignin per 100 phenyl propane units.

Functional Group	Abundance per 100 C ₉ units
Carbonyl	10-15
Benzyl alcohol	15-20
Phenolic hydroxyl (free)	15-30
Methoxyl	92-96

The nature of the lignin polymerization reactions results in the formation of a three-dimensional, highly-branched, interlocking network of essentially infinite molecular weight. Figure 5 is a schematic representation of a softwood lignin proposed by Adler [11] and later modified by Karhunen *et al.* This model was constructed based on the analysis of various linkages and functional groups. The phenylpropane (C₉ or C₆C₃) units in lignin are connected by C-C and ether (C-O-C) linkages. The frequency of such linkages is believed to have significant consequences on the lignin's overall reactivity toward the delignification process. It is important to note that the model proposed by Adler and Karhunen *et al.* does not depict the actual structure of lignin. Instead, it serves as a tool to visualize the linkages and functional groups believed to occur in lignin.

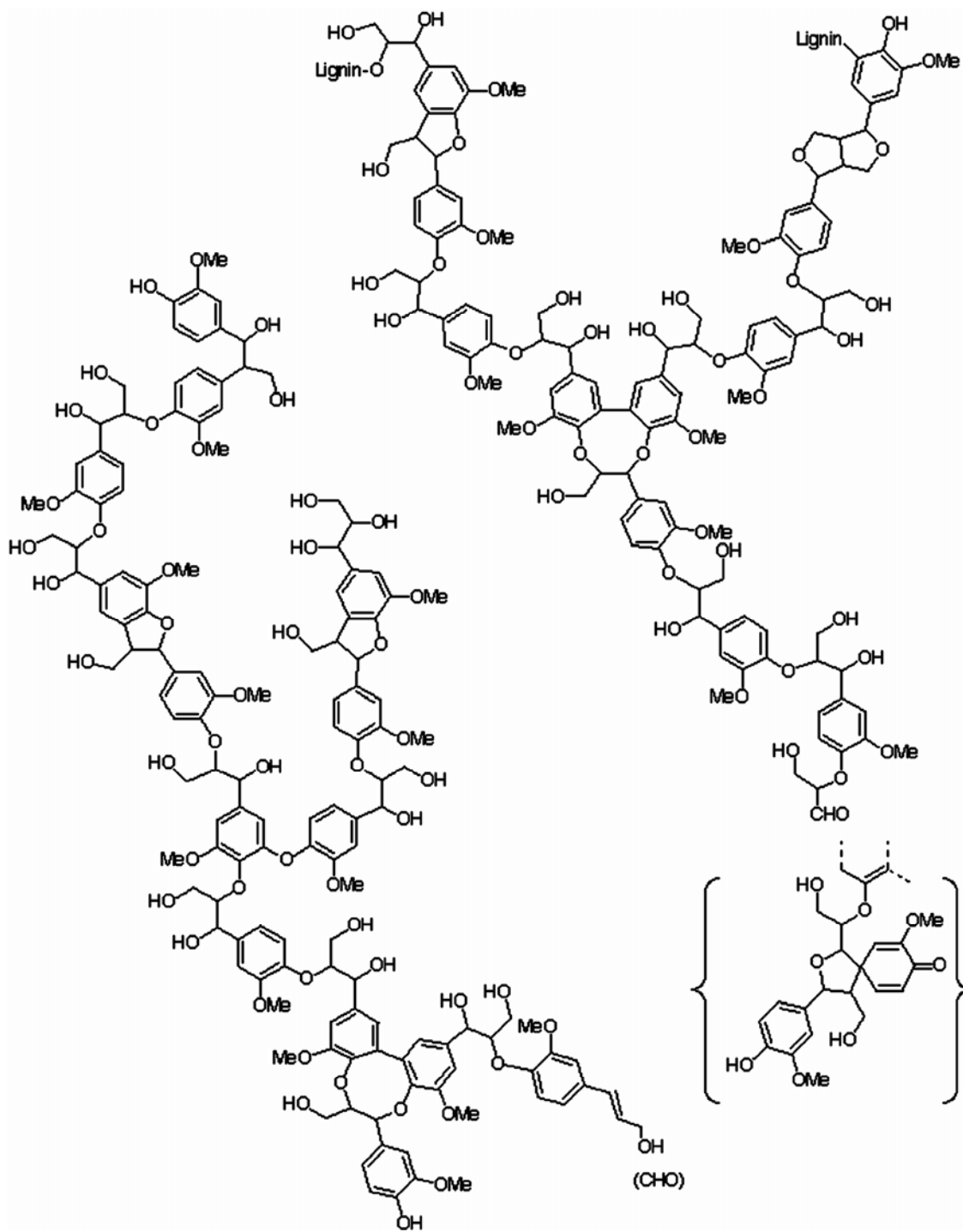


Figure 5. Structural model of softwood lignin.

Studies have also suggested that covalent linkages between lignin and hemicelluloses exist in native wood [12, 13]. These structures are typically referred to as lignin-

carbohydrate complexes or simply LCCs. The lignin is covalently bound to the hemicellulose which, in turn, is bound to cellulose through extensive hydrogen bonding. Lignin-carbohydrate complexes could be very important when considering pulping of wood since lignin is chemically bound to the cellulose.

Literature

- 1 Sarkanen, K.V. and Ludwig, C.H. Lignin: Occurrence, Formation, Structure and Reactions. ed. Sarkanen, K.V. and Ludwig, C.H. Wiley-Interscience: New York. 916 pp. (1971).
- 2 Sjöström, E. Wood Chemistry: Fundamentals and Application. Academic Press: Orlando. 293 pp. (1993).
- 3 Pearl, I.W. The Chemistry of Lignin. Marcel Dekker, Inc.: New York. 339 pp. (1967).
- 4 Freudenberg, K. and Neish, A.C. Constitution and Biosynthesis of Lignin. ed. Springer, G.F. and Kleinzeller, A. Springer-Verlag: New York. 129 pp. (1968).
- 5 Karhunen, P.; Rummakko, P.; Sipilä, J.; Brunow, G. and Kilpeläinen, I.; Dibenzodioxocins; A Novel Type of Linkage in Softwood Lignins. *Tetrahedron Letters* **36** (1). p. 167-170. (1995).
- 6 Karhunen, P.; Rummakko, P.; Sipilä, J.; Brunow, G. and Kilpeläinen, I.; The Formation of Dibenzodioxocin Structures by Oxidative Coupling. A Model for Lignin Biosynthesis. *Tetrahedron Letters* **36** (25). p. 4501-4504. (1995).
- 7 Karhunen, P.; Mikkola, J.; Pajunen, A. and Brunow, G.; The behavior of dibenzodioxocin structures during alkaline pulping processes. *Nordic Pulp and Paper Research Journal* **14** (2). p. 123-128. (1999).
- 8 Argyropoulos, D.S.; Jurasek, L.; Kristofova, L.; Xia, Z.; Sun, Y. and Palus, E.; Abundance and reactivity of dibenzodioxocins in softwood lignin. *Journal of Agricultural and Food Chemistry* **50** (4). p. 658-666. (2002).
- 9 Froass, Peter M.; Ragauskas, Arthur J.; Jiang, Jian-er. Chemical structure of residual lignin from kraft pulp. *Journal of Wood Chemistry and Technology*, **16**(4), 347-365 (1996).

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- 10 Kukkola, E.M.; Koutaniemi, S.; Poellaenen, E.; Gustafsson, M.; Karhunen, P.; Lundell, T.K.; Saranpaae, P.; Kilpelainen, I.; Teeri, T.H. and Fagerstedt, K.V.; The dibenzodioxocin lignin substructure is abundant in the inner part of the secondary wall in Norway spruce and silver birch xylem. *Planta* **218** (3). p. 497-500. (2004).
 - 11 Adler, E.; Lignin - Past, Present and Future. *Wood Science and Technology* **11** (3). p. 169-218. (1977).
 - 12 Björkman, A.; Studies on Finley Divided Wood Part 3. Extraction of Lignin-Carbohydrate Complexes with Neutral Solvents. *Svensk Papperstidning* **60** (7). p. 243-251. (1957).
 - 13 Eriksson, O. and Lindgren, B.O.; About the Linkage Between Lignin and Hemicelluloses in Wood. *Svensk Papperstidning* **80** (2). p. 59-63. (1977).