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LIGNIN PRODUCTION AND DETECTION IN WOOD

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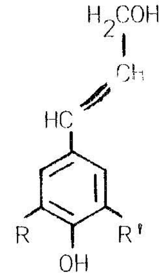
Within the past 10 to 20 years, biochemists and organic chemists have managed to find out much about how the cell walls are produced in growing plants. Atmospheric carbon dioxide is absorbed through the plant leaves and, by the action of light and chlorophyll in the process of photosynthesis, is activated in such a way that its carbon is combined with water to form carbohydrates. These simple sugars are polymerized in the plant to form long polysaccharide chains which are intertwined to make up the plant fibers: the pentoses, xylose and arabinose, and the hexoses, glucose, mannose, and galactose, give rise to the hemicelluloses, while β-glucose alone gives rise to cellulose.

Plants whose cell walls contain only layers of these polysaccharide fibers are soft and pliable like fresh grass or lettuce. A large plant, such as a tree, bush, or cornstalk, would not be strong enough to grow so high or to withstand winds, rain, and snow unless its polysaccharide walls were strengthened. That is why the plant makes lignin and deposits it in a hard paste around the elastic polysaccharide fibers to bind them together strongly. The enzymes in the plant cells take the simple sugars from the Calvin photosynthesis cycle and change them, via the aromatic a-amino acids L-phenylalanine and L-tyrosine, into the p-hydroxycinnamyl alcohols, p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (see formulas). Mixtures of these simple compounds are dehydrogenated by enzymes called phenol oxidases and condensed into an amorphous high polymer of very complicated structure, which cements the weak polysaccharide fibers together. It is this polymerization to produce lignin that makes a plant "woody."

$R = R' = H$ - p-Coumaryl alcohol

$R = H, R' = OCH_3$ - Coniferyl alcohol

$R = R' = OCH_3$ - Sinapyl alcohol



The two kinds of polymers in the plant cell walls are very different in nature. The polysaccharides are long chain molecules, with simple sugar units linked end to end as in a string of pearls. This is why they form long, pliant fibers easily. Lignin, on the other hand, has many different kinds of linkages between its constituent monomers and contains lots of branching points, so that it forms a cross-linked amorphous paste, something like putty. It is easy to see that strings of pearls embedded in hardened putty could no longer be bent or twisted. This is exactly what happens to the pliant polysaccharide fibers in the plant cell walls when they become lignified, i.e. encrusted by lignin.

When cellulose fibrils are required from wood for the production of paper or artificial silk (rayon, cellulose acetate), the insoluble lignin "putty" must be dissolved by drastic treatment with strong pulping chemicals. About 50 million tons of lignin are produced annually in the world as a waste byproduct of wood pulping. Because there are insufficient useful outlets for this material, most of it must be burned to avoid water pollution in its disposal.

It is easy to detect lignin chemically, for example, in a piece of softwood or in a sheet of low-grade paper such as newsprint, by dabbing the sample alternately with (1) a 1 percent solution of phloroglucinol in alcohol and (2) concentrated hydrochloric acid. A brilliant red color develops, owing to the presence of coniferaldehyde groups in the lignin. This Wiesner test is often used by botanists to detect lignin in plant tissues.

Hardwoods (from deciduous trees) and softwoods (from conifers) can be differentiated using the Mäule test because of differences in their lignins. Wood treated with dilute chlorine water (or in series with 1 percent potassium permanganate solution, wash water, and concentrated hydrochloric acid) gives a red color with concentrated ammonia solution if derived from a hardwood species, but only a dirty brown color if derived from a softwood species. The red color is due to the higher content of units derived from sinapyl alcohol in hardwoods.

The lignin polymer contains aryl alkyl ether as one of the weakest types of link between its constituent C_6-C_3 units. These are split by the sulfur chemicals or alkali used at high temperatures during pulping, thus breaking down the polymer into smaller fractions. The phenolic hydroxyl groups in lignin, plus the sulfonic acid groups ($-SO_3H$) introduced into the degraded lignin molecules during pulping, help to make the material soluble in the alkaline pulping liquors. When the lignin is dissolved from the wood in this way by pulping, the unaffected cellulose fibers (pulp) are released and can be collected and washed or bleached free from residual lignin. The freer the pulp from lignin, the better the quality of the paper that can be produced from it. Hardly any lignin is removed from newsprint, so that is why the Wiesner color test for lignin works so well with it.