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Lignin and Lignans. Advances in Chemistry

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Since the realization of global sustainability depends on renewable sources of materials and energy, there is an ever-increasing need to use plant biomass to develop bio-based goods able to replace petroleum-based one.

Biomass crops, woody species or grasses consist primarily of cell walls, composed of a complex matrix in which cellulose are embedded in a network of cross-linking hemicellulose polysaccharides. *Lignin* acts to harden the wall, providing structural rigidity and a physical barrier to fungi and insects, and assists movement and transport of water in plants.

As complex compound, it forms a barrier for evaporation, helping to channel water to critical areas of the plant and, while its content and structure that depends on the type of tree, can vary within the same plant. Furthermore, lignin has an interesting redox potential containing more diverse reactive chemical groups, such as aromatic and aliphatic hydroxyl, carboxyl, and carbonyl moieties. However, it is a polymer that, built up by the combination of three basic monomer types (p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol), is formed from oxidative coupling of hydroxycinnamyl alcohols and related compounds such as hydroxycinnamaldehydes.

The polymerization which occurs in the cell wall, especially in the secondary cell walls at the level of the water-conducting xylem vessels and sclerenchyma fibers, is mediated by peroxidases and/or laccases. Variation in lignin composition is a function of plant species, age, and tissue type. However, it is interesting to remember that lignin has historically been viewed as a waste product with little intrinsic value, while today, with the desire to maximize the use of all components of the biomass, efforts are being made to identify additional uses of this interesting polymer also.

For all these considerations and because of the increasing economical interest to the global use of plant biomass, a deeper knowledge of lignin's chemistry has to be taken in great consideration. This the scope of *Lignin and Lignans*.

The goal of this book, comprised of **17 Chapters**, is to provide a source for reporting an update knowledge of *lignin* in the key areas of more specific interest.

Due to its complexity, non-uniformity, and conjunctive bonding to other compounds, *lignin* has been difficult to isolate for determining its structure, and converting this complex compound in useful consumer products.

Chapters 1 and **8** give the reader a coherent picture of lignin properties reporting data on its thermal stability and molecular motion when isolated. It is difficult, in fact, to measure a single component in a biocomposite such as wood, since it contains three macromolecular species: cellulose, hemicellulose, and lignin. X-ray diffractograms indicate that the isolated lignin, frozen in the glassy

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state (i.e. a nonequilibrium state) is represented by a broader distribution of structures in comparison with synthetic polymers, such as polystyrene. Moreover the molecular motion of hydrophilic polymers is enhanced in the presence of water. Water molecules break intermolecular hydrogen bonds and make segmental motion occur easily.

However, the molecular motion of lignin, having phenyl groups in the main chain, is similar to that of synthetic polymers but because of the presence of many hydroxyl groups, its motion is influenced by the hydrogen bonds water molecules. In any way, the real problem with the structural studies is to obtain a sample of lignin not been significantly altered by its isolation from the other plant components. This polymer seems not to be a stand-alone polymer, but has linkages to polymeric carbohydrates. Some data of *in situ* lignin are, however, discussed according to results that have recently been obtained using new methods, such as thermal analysis and viscoelastic measurements.

One of the greatest challenge in the structural biochemistry of the lignified cell wall is to determine the nature and proportion of building units and interunit linkages in native lignin structures. Thus Chemical and spectral structural studies are reported from **Chapter 2** to **7**.

Lignins are essentially composed of C_6C_3 units, namely p-hydroxyphenyl (H), guaiacyl (G), and syringyl(S) units, in various proportions, according to botanical, physiological, and cytological criteria. These units are interconnected by a series of carbon-oxygen(ether) and carbon-carbon linkages in various bonding patterns. Moreover, there is a universal consensus for the predominance of the labile Beta-O-4 ether linkages in native lignins, as well as the occurrence of the more resistant Beta-5, 5-5, Beta-Beta, 5-O-4, and Beta-1 interunit linkages, and the advent of sophisticated nuclear magnetic resonance (NMR) techniques has greatly aided the understanding of lignin structure.

The real unsolved problem is to obtain lignin samples not significantly altered by their isolation from the other plant components, also if the chemical degradation methods will continue to have an important role in lignin research. Thus, the electronic spectra of lignin and lignin model compounds can be adequately understood by examining the substituent effects on the three bands of benzene. On one hand improvements in instrument design and the wide availability of microcomputers studies have confirmed the importance of quinone structures to the colour of wood and pulps, clarifying their response to the common bleaching agents. On the other hand , the transient spectroscopy and emission spectroscopy have clarified the spectra and chemistry of the excited electronic states of lignin.

Another important tool in modern chemistry is vibrational spectroscopy evidenced by three important methods: Raman spectroscopy, infrared spectroscopy (IR), near-infrared spectroscopy (NIR). In organic molecules, in fact, vibrational spectra arise from two different types of energy exchanges between the molecules under study and the electromagnetic radiation. In infrared spectroscopy, a vibrational transition that involves a change in dipole moment results in absorption of an infrared photon. The energy of the absorbed photon is equal to the different energy occurring between the two vibrational states of the molecule. It is therefore possible to correlate the well-defined frequencies at which certain bond types of carbon, hydrogen, and oxygen are expected to absorb or scatter.

Thus, it is important to consider the types of functional groups that occur in lignin, together with their structural variations, correlating the characteristic absorption of each single bond with the collective properties of the clusters' bonds of the aromatic centers by the use of these techniques.

However, NMR has enormously facilitated the investigations into of lignin structural aspects, playing the major role in the qualitative and quantitative understanding of its structure, because of the high resolution and the high dispersion of its chemical shifts. In any way the selective and quan-

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titative tagging of lignin, followed by quantitative NMR data acquisition, has the potential to provide some truly unique insights toward understanding the complex and variable reactions of lignin under conditions of natural or commercial transformations, also if its true quantification remains difficult because of the signal overlap and other factors. The best quantitative method remains, therefore, the relatively tedious inverse-gated technique, along with an internal standard substance. But with molecules like lignins there are few guidelines and there are no absolutes, so that any value obtained from a nonquantitative technique must be compared to a corresponding value obtained from an inverse-gated experiment to determine its quantitative validity.

Lignin/lignan reactions are reported in **Chapters** from **9** to **15**. The complex and variable structure of lignin in wood and pulp, combined with the morphology of wood-derived fibers, have stimulated research in the areas of pulping and blenching, amply reported and discussed in these chapters according to their different and challenging aspects. The mechanical and chemical processes remain, however, the most widely used in today's pulp and paper industry being actually the less expensive. Nevertheless, there has been an increase of new engineered productive bioprocesses competing with the conventional chemical and mechanical methodologies, due to the rapid advances in biotechnology and molecular biology, the dramatic improvements in computational chemical methods, the marked increase in the understanding of the mechanisms of fungal and enzymic pulping and biobleaching, and the rapidly growing of database of fungal genomes.

Mechanical pulping, in fact, needs much energy and also does not preserve the quality of the product, while biological pulping by use of lignin-decomposing fungi such as *Phanerochaete chrysosporium, Pholiota mutabilis, Tremetes versicolor, and Phlebia spp* is a finding application in the paper industry because of the better results for the quality obtained.

In contrast with cellulose and hemicellulose, lignin is the only polymeric component of the plant fiber that absorbs both visible and near-UV light, because of the presence of quinones and catechols in its molecule. During the productive process of pulping, the photooxidation of lignin causes depolymerization through cleavage of interunit bonds and yellowing through the oxidation of the aromatic groups.

Chapter 6 describes the results of researches elucidating the detailed reaction pathways leading to photodegradation and chromophore formation. Lignin, in fact, undergoes photooxidative degradation through two mechanisms. One involves excitation followed by abstraction oh hydrogen, which is followed by addition of ground-state triplet oxygen to carbon-based radicals to form hydroperoxides. The other mechanism is sensitizing the formation of singlet oxygen that undergoes electrophilic addition to the aromatic rings. Both free radicals and singlet oxygen produced inside the fiber wall degrade the macromolecule lignin.

By far, the principal use of lignin is as fuel in the production of pulp used for paper and corrugated board, due to its high calorie content, which make it excellent for this purpose.

Moreover, for its carbohydrate component some plants are now being processed for ethanol fuel production also. However, the many pharmacological properties of lignans have not been forgotten from the authors of this interesting book.

This is the interesting topic of **Chapter 17**. Lignans and neolignans are natural products derived from the same phenylpropane units that make the lignin polymer; many of them, isolated from medicinal plants and identified, have shown a variety of biological activities having, for example, antiinflammatory, antioxidant, antibacterial or hypolipidemic activity, as well as antiallergy, analgesic or

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hypotensive effect etc. These and many other pharmacological activities are amply reported and discussed in this final chapter.

As previously reported, plant biomass is a renewable resource that causes problems when not used. The challenge, therefore, is to convert biomass as a resource for energy and other productive uses, identifying and assess environmentally-sound technologies and goods. Overall the necessity to raise awareness on the waste raw material use globally, especially in the developing countries, enable the implementation of technologies to reduce *greenhouse gas* emissions from the use of fossil fuels, and augment material resources for a variety of products. One purpose of this book is to give the necessary chemical information to decision-makers and end-users in selecting plant biomass conversion by knowledge and technologies. Hence, the development of efficient and cost-effective processes for the synthesis of biopolymers or renewable goods is a key requirement for the gradual replacement of petroleum-based chemicals and materials.

This will require a deep knowledge on the chemical composition of lignin and lignans together with flexible plant designs that can adapt to varying needs and demands. In addition, the pre-treatment method, amply described on this book, is a crucial factor governing the quality of cellulose, hemicellulose and lignin fractions from the bio-refinery processes, and therefore the potential value-added bio- products that can be produced.

Continuing knowledge and investments in academic and private research efforts for the development of a mature bio-products industry. Widespread societal adoption of bio-energy and bio-based products will require education of the general public, as well as environmental and economic policies, encouraging the transition from fossil to renewable resources, such as lignin and lignans.

This is the reason why this book has to be in the library of scientists working in academic and industrial research laboratories, interested not only on the field of Organic chemistry, Analytical chemistry, Engineering chemistry, Biochemistry, and Pharmacology, but also for people interested in Cosmetic Dermatology, Industrial processes and Environmental problems.

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