1 Overview

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CONTENTS

INTRODUCTION

As the second most abundant natural polymer in our world, lignin has drawn the attention of many scientists for several centuries. Due to its complexity, nonuniformity, and conjunctive bonding to other substances, lignin has been difficult to isolate without modification and difficult to convert into useful consumer products, and its structure has been difficult to determine. The challenges presented in studying lignin have resulted in a vast amount of published literature. The goal of this volume is provide a resource that summarizes our present knowledge of lignin in certain key areas. The most inclusive description prior to this volume is best summarized in the book of K. V. Sarkanen and C. H. Ludwig, *Lignin* (Wiley-Interscience, 1971). This overview chapter takes much of its material from the aforementioned book and invites the reader to consult this book for greater depth. No references are presented in this first chapter; most discussion is supported by material in Sarkanen and Ludwig's book.

The biosynthesis of lignin is an important subject to understanding lignin structure, but it is not covered in this volume. It is a topic that deserves separate treatment, is steeped in controversy, and would add approximately 50% more pages to an already large volume. This volume focuses mainly on modern methods of lignin structure proof, on lignin reactivity, and on one aspect of lignan use. This brief introductory chapter is intended to familiarize the reader with a few basics, which are inherent to the discussions of the later chapters.

The discussion presented in this chapter will be expanded with the material given in Chapter 8. The layout of the volume is to present (i) a simple picture in this chapter; (ii) detailed chemical and spectral structural studies in Chapters 2–7; (iii) a coherent picture of lignin structure in Chapter 8; (iv) lignin/lignan reactions in Chapters 9–15, and then (v) pharmacological properties of lignans in Chapter 16. Since some readers will jump around from one chapter to another, we will (out of necessity) have some

repetition of material. In general, a reader will better understand the chemistry presented in later chapters by first reading the earlier chapters, especially Chapters 1 and 8.

OCCURRENCE

Nature is composed of minerals, air, water, and living matter. The latter contains polymers. The most abundant natural polymer is cellulose. It, together with lignin and hemicelluloses, are the principal components of plants. The principal function of lignin in plants is to assist in the movement of water; the lignin forms a barrier for evaporation and, thus, helps to channel water to critical areas of the plant.

Lignin is present in plants for which water conduction is important. Of greatest interest is its presence in trees. The lignin content depends on the type of tree: about 28% for softwoods and 20% for hardwoods. The cellulose content is approximately 45% in the wood of both types, while the hemicellulose content is roughly 17% in softwoods and 25% in hardwoods. Lignin structure can vary within the same plant, e.g., primary xylem, compression wood, early versus late wood, etc.

FORMATION AND STRUCTURE

Lignin is a polymer, built up by the combination of three basic monomer types, as shown in Figure 1.1. These building blocks, often referred to as phenylpropane or C_9 units, differ in the substitutions at the 3 and 5 positions. (Note: Typical phenols would have a numbering system that makes the phenol carbon #1; however, lignin nomenclature assigns the side-chain attachment to the aromatic ring as #1 and the phenol carbon as #4. Consequently, for the sake of consistency, we will use lignin nomenclature rules for the building blocks.)

Figure 1.2 outlines the main functional groups and numbering in lignin. The attachment of the aliphatic side chain to the aromatic ring is at C–1. The phenol oxygen is attached at C–4 and the numbering around the ring follows a rule that you use low numbers, which means that if there is only one methoxyl group it will be on C–3 (not C–5). The side-chain carbons are designated α, β, and γ, with C–α being the one attached to the aryl ring at its C–1 position. Not shown in Figure 1.2 are the possible occurrences of aliphatic and aryl ether linkages at C–α and C–γ, and ester

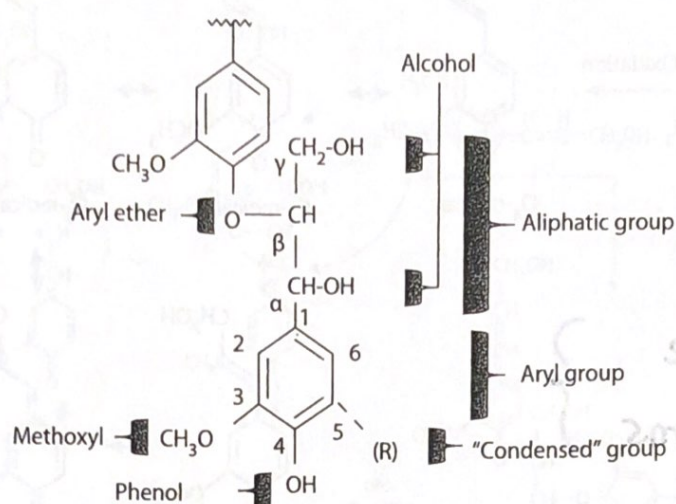| Substituents	Name	Location
R = R' = H	p-coumaryl alcohol	Compression wood, grasses
R = H, R' = OCH$_3$	coniferyl alcohol	Hardwoods and softwoods
R = R' = OCH$_3$	sinapyl alcohol	Hardwoods

FIGURE 1.1   Lignin monomeric building blocks.

FIGURE 1.2 Lignin functional groups.

linkages at C–γ to non-lignin carboxylic acid groups. The existence of a carbon group at C–5 is often referred to a "condensed" structure. The term *condensed* is used rather loosely, being applied to both native and C–5 linkages formed during lignin reactions.

The principal monomer for softwood lignins is coniferyl alcohol, which has a methoxyl group on the C–3 position. Hardwood lignins have two main monomers: coniferyl alcohol and sinapyl alcohol, which has methoxyl groups on both the C–3 and C–5 positions. The third monomer, p-coumaryl alcohol, is more prominent in grasses and compression wood (branch conjunctures). The aromatic rings of the monomers are often referred to as follows: **guaiacyl** units have one aryl-OCH_3 group and are derived from coniferyl alcohol, **syringyl** units have two aryl-OCH_3 groups and are derived from sinapyl alcohol, and **p-hydroxyphenyl** units have no OCH_3 groups and are derived from p-coumaryl alcohol.

Native lignin arises via an oxidative coupling of the aforementioned alcohols with each other and (more important) with a growing polymer end unit. The oxidation produces a phenolic radical with unpaired electron density delocalized to positions O–4, C–1, C–3, C–5, and C–β; Figure 1.3 shows an example set of resonance forms for coniferyl alcohol. The lignin polymer can be initiated by coupling of two monomeric radicals, but more likely grows when monomer radicals couple with phenoxy radicals formed on the growing polymer. The phenoxy C–β position appears to be the most reactive, since the most abundant linkages in lignin involve this position (β–O–4, β–5, β–β).

An example of an oxidative coupling of coniferyl alcohol, which generates the abundant β–O–4 bond, is shown in Figure 1.4. The scheme is greatly simplified, since (a) only individual radical forms of the phenoxy radical are shown; (b) monomer-monomer coupling is shown, rather than the more prevalent monomer to polymer coupling process; and (c) the alcohols are likely conjugated with carbohydrates. Quinone methide intermediates from one coupling can participate in further coupling as the polymerization proceeds. Note, the term "quinone methide" refers to a nonaromatic structure that
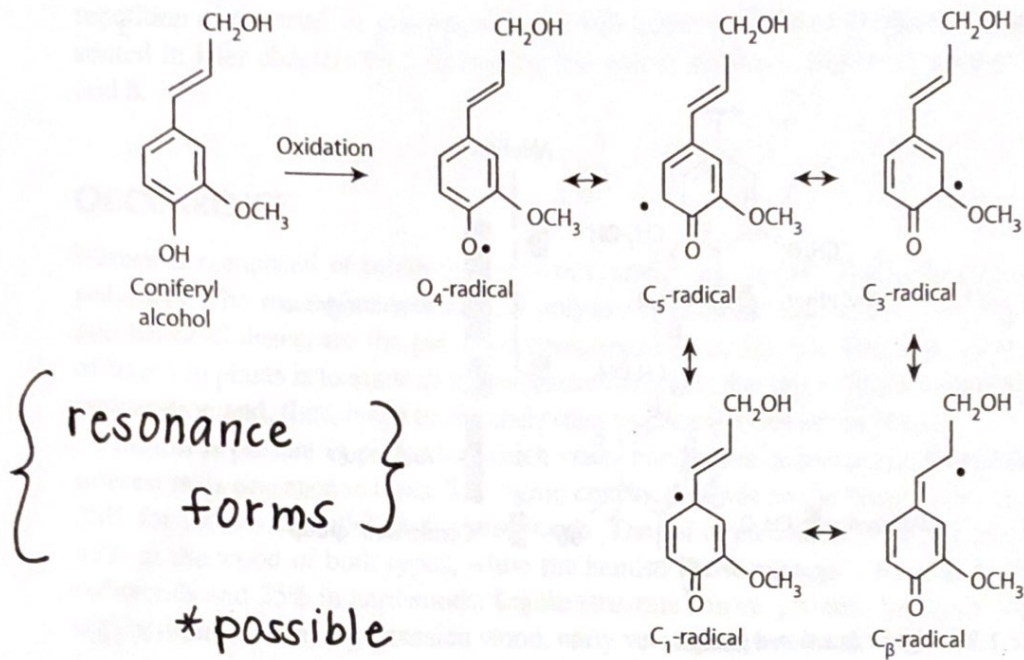
FIGURE 1.3 First step in lignin softwood polymerization.
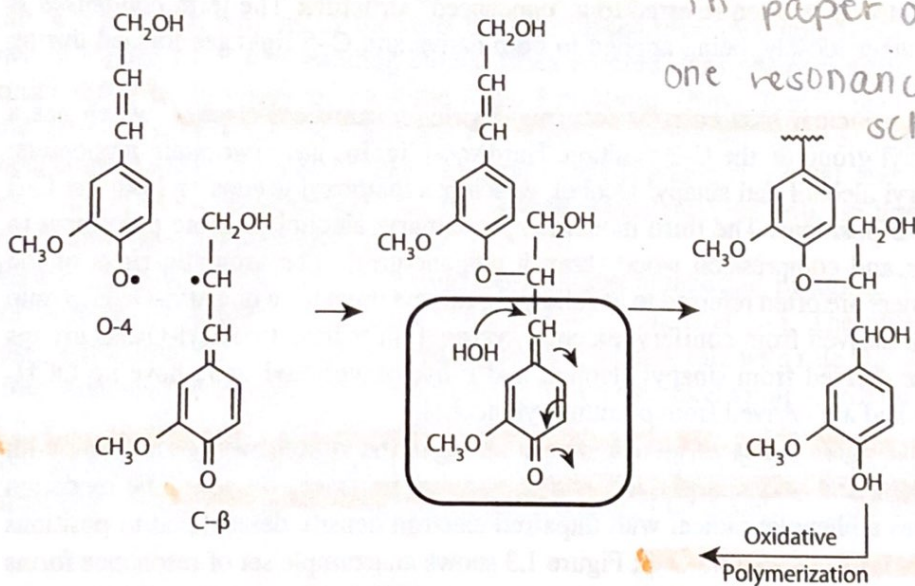
*include figure in paper of one resonance scheme!

FIGURE 1.4 C_β–O_4 bond formation via radical coupling.

has two double bonds exiting the ring between $C_1 = C_\alpha$ and $C_4 = O_4$. These quinone methides are quite reactive and readily accept additions of nucleophiles to the $C_1 = C_\alpha$ double bond, resulting in regeneration of a much more stable aromatic ring, as shown by the chemistries presented in Figures 1.4 through 1.8.

In addition to the formation of β–O–4 and α–O–4 ether bonds, as shown in Figures 1.4 and 1.5, an ether linkage between C–5 and O–4 (a diphenyl ether) is
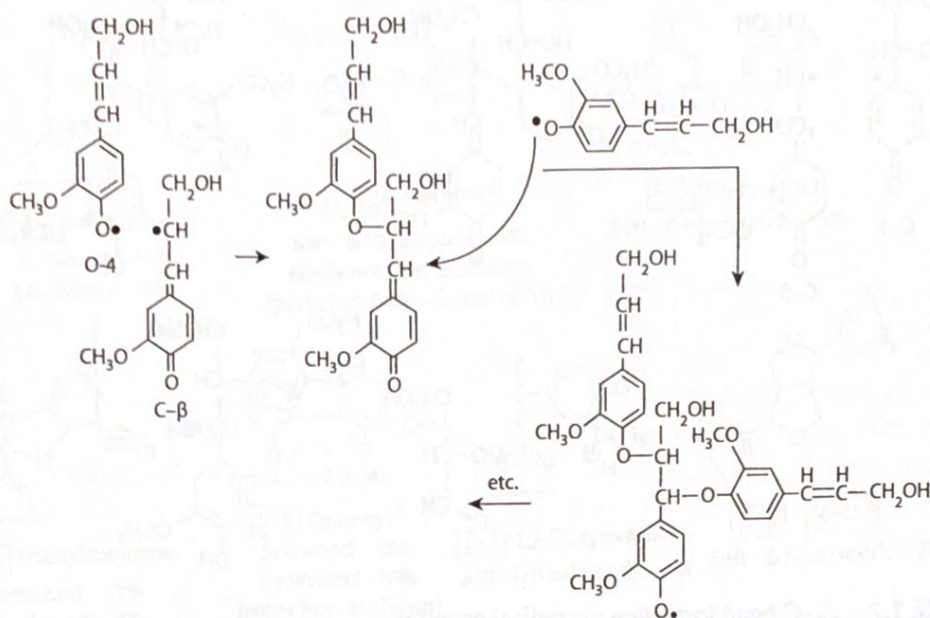
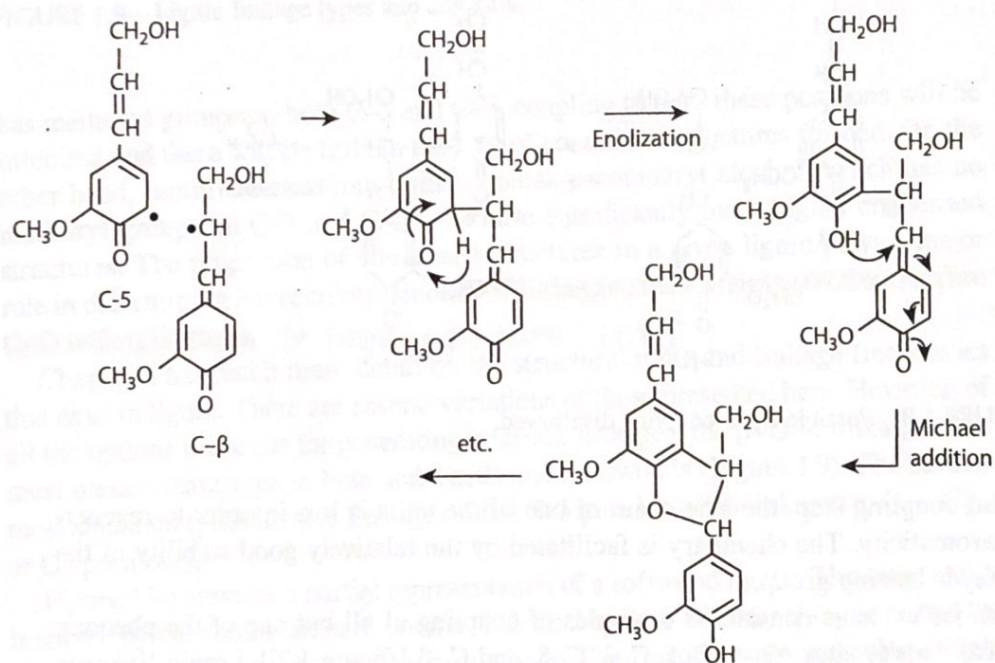**FIGURE 1.5** C_α–O_4 bond formation via radical coupling.

FIGURE 1.6 C_5–C_β bond formation via radical coupling.

also present to a small extent in lignin. Several C–C linkages also exist; Figure 1.6 outlines the chemistry for the production of a β–5 linkage. The latter is an example of a naturally occurring condensed structure. Another common C–C linkage in lignin exists in biphenyl units, which occur by the coupling of two phenoxy radicals at their C–5 positions. Coupling of a phenoxy radical at the C–1 position is also possible, an example of which produces a β–C–1 linkage (Figure 1.7). After the

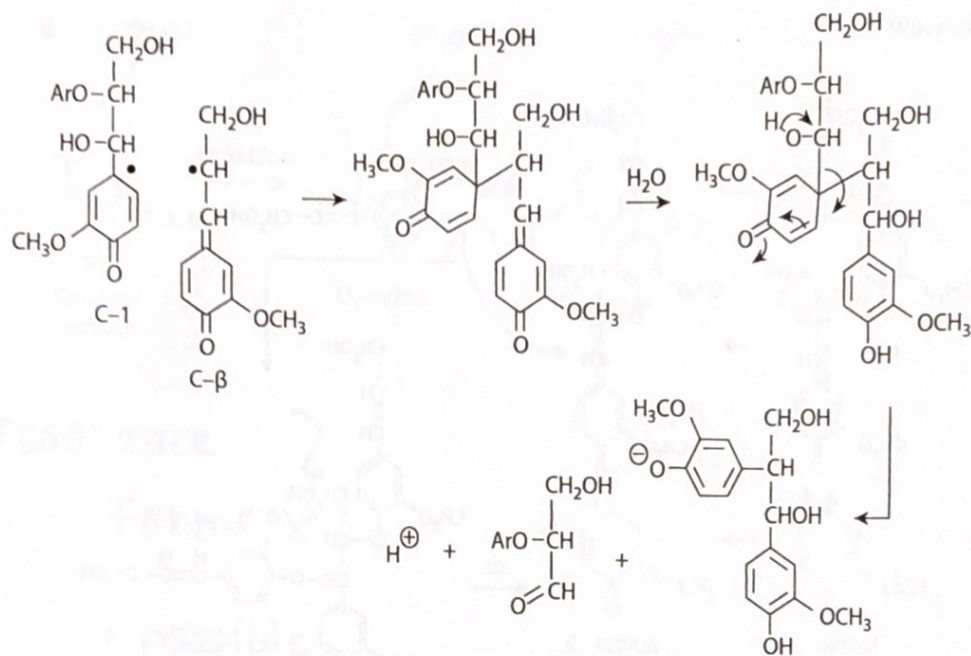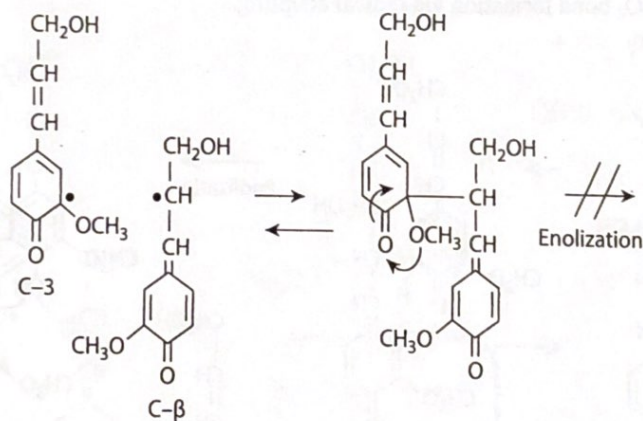**FIGURE 1.7** C_1–C bond formation via radical coupling.

FIGURE 1.8 Possible C_3–C coupling disallowed.

initial coupling step, the side chain of one of the units is lost in order to regenerate aromaticity. The chemistry is facilitated by the relatively good stability of the aldehyde leaving group.

So far we have considered examples of coupling of all but one of the phenoxy radical density sites (O–4, C–1, C–3, C–5, and C–β [Figure 1.2]). Lignin linkages involving the C–3 site have not been observed. Coupling at this position likely occurs, but the process does not lead to a stable product (Figure 1.8). There is no good way for the aromatic ring to be regenerated with the methoxyl group present at C–3, since it is a poor leaving group. Consequently, the coupling likely reverses back to the individual radical species, which find other ways to couple, such as those shown in Figures 1.4 through 1.7. Since the building block sinapyl alcohol
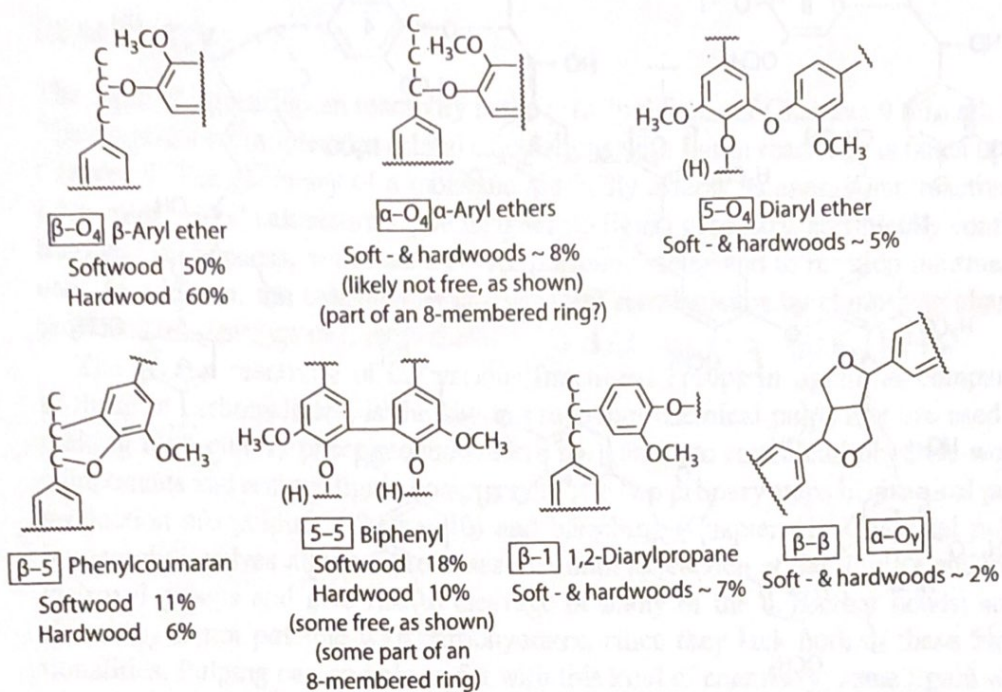
FIGURE 1.9 Lignin linkage types and amounts.

has methoxyl groups on both C–3 and C–5, coupling to both these positions will be inhibited and there will be little in the way of condensed structures formed. On the other hand, lignin derived from building block p-coumaryl alcohol, which has no methoxyl groups on C–3 and C–5, will have significantly more highly condensed structures. The proportion of condensed structures in a given lignin plays a major role in determining its reactivity, since C–C linkages are much less reactive than are C–O (ether) linkages. ✳ look up more info!

Chapter 8 has much more detail on the structural units and linkage frequencies that exist in lignin. There are several variations of those presented here. However, of all the options that exist for generating interunit linkages, the β–O–4 linkage is the most predominant type in both softwoods and hardwoods (Figure 1.9). The second most abundant types involve linkages to the C–5 position (with linkages to C_β–, C_5–, or O_4-positions).

Figure 1.10 presents a partial representation of a softwood lignin. The main chain is shown by the combination of coniferyl alcohol units 1–10. Branching is shown by the units A and C attached to the main chain. The linkage types are color coded: dashed lines = more reactive ether bonds, dotted lines = low reactive C–C and O–4/ C–5 ether bonds, and dashed and dotted lines = the generally reactive α–O–4 and α–O–γ bonds. It should be pointed out that this picture is an oversimplification; the picture will be further refined as the reader delves into the various chapters. The message intended to be conveyed now is that lignin is a complex cross-linked polymer made up of different monomer units, linked in a variety of ways. Lignin exhibits a wide polydispersity, meaning that it has no characteristic molecular weight; values of 400 to more than a million weight average molecular weight have been reported.

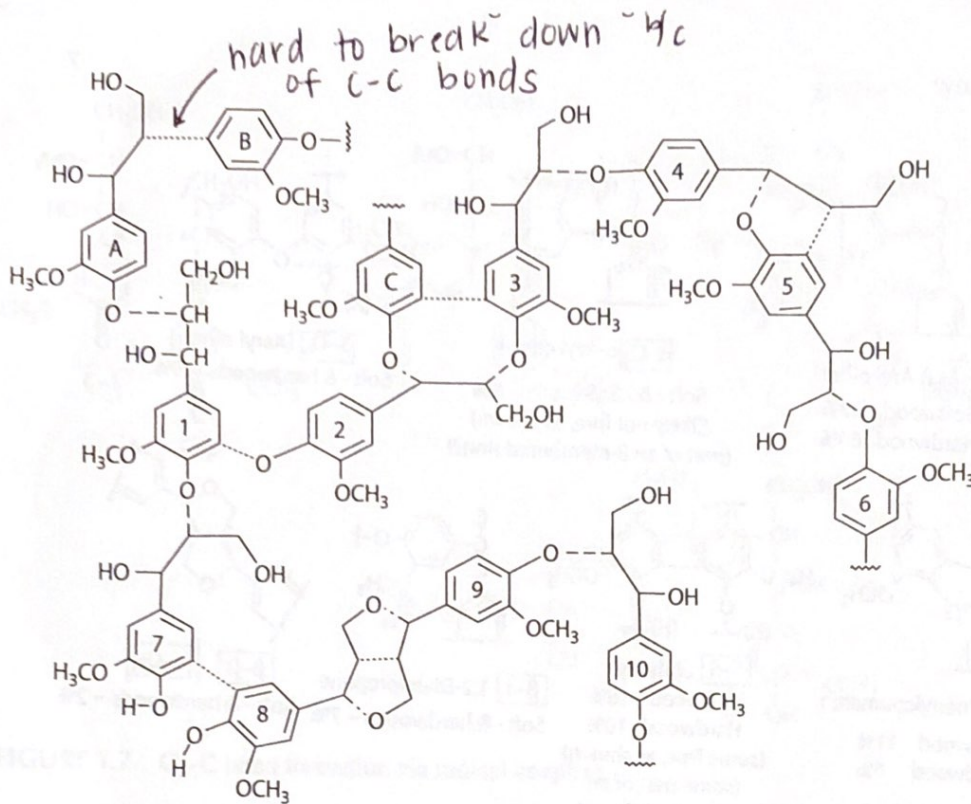*hard to break down 4c of c-c bonds* (handwritten annotation)

FIGURE 1.10 Example lignin structure.

ISOLATION AND STRUCTURE PROOFS

How have scientists defined such a complex substance? The answer is as complex as lignin itself and is still under active investigation. Early lignin studies involved isolating a lignin sample, degrading the polymer into small pieces, and deducing the polymer structure from the identity of the pieces. This was extremely tedious work. Newer methods, such as thioacidolysis, in combination with gas chromatography-mass spectroscopy, have been valuable tools in the determination of the lignin-derived monomers (Chapter 2). The advent of sophisticated nuclear magnetic resonance (NMR) techniques has greatly aided the understanding of lignin structure (Chapters 5 and 6). In addition, further structural insights are possible by the use of other spectral techniques (Chapters 3 and 4) and by thermal analysis (Chapter 7). 8

A real problem with all of these structural studies is to obtain a lignin sample that has not been significantly altered by its isolation from the other plant components. Research has made it clear that lignin is not a stand-alone polymer, but has linkages to polymeric carbohydrates. These unions are referred to as "lignin-carbohydrate complexes" (Chapter 8). Much will be said about the issues of isolation in the upcoming chapters. 7

To aid in the study of native lignin, researchers have prepared synthetic lignins, referred to as dehydrogenation polymers (DHP), by mixing lignin building blocks with oxidative enzymes. The DHPs can be obtained without interferences from other wood components, providing a baseline sample for comparison to structural analysis of native lignin.

REACTIVITY

The topic of lignin/lignan reactivity is the principal focus of Chapters 9 through 15. The correlation of molecular orbital calculations with lignin reactivity is taken up in Chapter 9. The geometry of a molecule markedly affects its energy and reactivity. Molecular orbital calculations give insight into lignin geometry, specifically conformational preferences, with respect both to ground states and to reaction intermediates. In addition, the calculations can pinpoint reactive sites by computing charge (and radical) densities of intermediates.   *did using ESR/EPR

The greater reactivity of the various functional groups in lignin, as compared to those in carbohydrates, is the key to producing chemical pulps that are used in making high-quality paper products. Here the goal is to retain carbohydrate wood components and remove lignin components. The two primary steps in chemical pulp production are pulping (Chapter 10) and bleaching (Chapter 11). Chemical pulping largely involves alkaline processes that initiate reaction at the lignin's phenolic hydroxyl groups and give rise to cleavage of many of the aryl ether bonds; such chemistry is not possible with carbohydrates, since they lack both of these functionalities. Pulping can go only so far with this kind of chemistry; some lignin will still be resistant. This is where bleaching comes in. Here the chemistry involves breakdown of the lignin aromatic units, again a feature not present in carbohydrates. While this all seems simple enough, the reality is that there are many complexities, which will be the topics in Chapters 10 and 11.

.Lignin does not have to be totally, or even partially, removed to give rise to paper products. Examples include pulps produced by the mechanical defibration of logs and steamed and/or chemically treated chips. Such pulps still contain significant quantities of lignin and suffer from lower bleachability and yellowing due to thermal- and light-induced oxidation. However, such pulps can be produced with double the yield and one-quarter the pollution than that obtained by chemical pulping. In addition, it is advantageous to use lignin-rich pulps because of higher bulk that permits lower basis weight and larger printing surface per ton of paper. Chapters 12 and 13 report on the advances in the chemistry of oxidative and reductive lignin-retaining bleaching. Brightness is one of the most important parameters that determine value. The oxidation and reduction of colored chromophores in lignin-containing pulp (stone and refiner groundwood), sometimes in sequence, increases the value of the paper produced. Chapter 14 reports on the photochemical processes of lignin and lignin model compounds, most of which cause yellowing of high-brightness lignin-containing papers. Lignin contains both moieties that absorb light to produce free-radicals, and react with oxygen, and moieties that react with photo-induced radicals. Also, there are lignin groups that sensitize the formation of reactive singlet oxygen ($^1O_2$), which in turn react with the various groups in lignin to cause color production and contribute to β–O–4 aryl etheir cleavage.

An evolving area is the use of biodegradation as a means to facilitate lignin removal (Chapters 15 and 16). Useful biodegradation chemistry again takes advantage of existing reactivity differences between lignin and carbohydrates. The employed enzymes often have high specificity for phenolic structures.

USES

By far, the principal use for lignin is as fuel in the production of pulp used for paper and corrugated board. High-quality paper products require that the lignin be separated from the cellulose in wood. The pulping process produces a pulp rich in cellulose and a liquor rich in degraded lignin. The liquor is partially evaporated and burnt in a furnace. Inorganic pulping chemicals are recovered, and the energy generated is used in the pulp production. Lignin has a high calorie content, which makes it an excellent fuel. In essence, the lignin in wood provides the energy needed to make the cellulose-rich pulp. This sentence can be changed to the following: Bleaching follows pulping when high-brightness products are desired. The lignin-derived fragments in the bleaching liquors have no value and disposal of these liquors is a problem.

For many decades, researchers have tried to find applications for uses of lignin derived from pulping liquors. This highly altered, complex lignin presents real challenges with respect to finding commercially valuable end uses. However, the future use of plants (including wood) as sources of chemicals, rather than just for making paper products, will generate large quantities of a new kind of lignin. Some plants are now being processed for ethanol fuel production (from their carbohydrate components); commercial uses of the lignin by-product will greatly enhance the processing costs.

Chapter 17, Pharmacological Properties of Lignans, is the only chapter in this volume that specifically addresses uses and characteristics of lignans. This chapter describes the activity of a wide variety of lignans derived from medicinal plants and used in traditional and folk medicines. The chapter also reports on the physiological changes in tumors in the digestive, reproductive, and endocrine systems caused by lignans and how these effects can be incorporated into various therapies.

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