3 Cell Wall Chemistry

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In chemical terms, wood is best defined as a three-dimensional biopolymer composite composed of an interconnected network of cellulose, hemicelluloses, and lignin with minor amounts of extractives and inorganics. The major chemical component of a living tree is water, but on a dry-weight basis, all wood cell walls consist mainly of sugar-based polymers (carbohydrates, 65–75%) that are combined with lignin (18–35%). Overall, dry wood has an elemental composition of about 50% carbon, 6% hydrogen, 44% oxygen, and trace amounts of inorganics. Simple chemical analysis can distinguish between hardwoods (angiosperms) and softwoods (gymnosperms) but such techniques cannot be used to identify individual tree species because of the variation within each species and the similarities among species. In general, the coniferous species (softwoods) have a higher cellulose content (40–45%), higher lignin (26–34%), and lower pentosan (7–14%) content as compared to deciduous species (hardwoods) (cellulose 38–49%, lignin 23–30%, and pentosans 19–26%). Table 3.1 shows a summary of the carbohydrates, lignin, and ash content of hardwoods and softwoods in the United States (Pettersen 1984).

TABLE 3.1
Summary of Carbohydrate, Lignin, and Ash Compositions for U.S. Hardwoods and Softwoods

Species	Holocellulose	Alpha Cellulose	Pentosans	Klason Lignin	Ash
Hardwoods	71.7 ± 5.7	45.4 ± 3.5	19.3 ± 2.2	23.0 ± 3.0	0.5 ± 0.3
Softwoods	64.5 ± 4.6	43.7 ± 2.6	–9.8 ± 2.2	28.8 ± 2.6	0.3 ± 0.1

Source: Pettersen, 1984.

A complete chemical analysis accounts for all of the components of wood. Vast amounts of data are available on the chemical composition of wood. The tables at the end of this chapter (Table 3.13 and Table 3.14) summarize data for wood species in North America (Pettersen 1984).

3.1 CARBOHYDRATE POLYMERS

3.1.1 Holocellulose

The major carbohydrate portion of wood is composed of cellulose and hemicellulose polymers with minor amounts of other sugar polymers such as starch and pectin (Stamm 1964). The combination of cellulose (40–45%) and the hemicelluloses (15–25%) is called holocellulose and usually accounts for 65–70 percent of the wood dry weight. These polymers are made up of simple sugars, mainly, D-glucose, D-mannose, D-galactose, D-xylose, L-arabinose, D-glucuronic acid, and lesser amounts of other sugars such as L-rhamnose and D-fucose. These polymers are rich in hydroxyl groups that are responsible for moisture sorption through hydrogen bonding (see Chapter 4).

3.1.2 Cellulose

Cellulose is the most abundant organic chemical on the face of the earth. It is a glucan polymer of D-glucopyranose units, which are linked together by β-(1→4)-glucosidic bonds. The building block for cellulose is actually cellobiose, since the repeating unit in cellulose is a two-sugar unit (Figure 3.1).

The number of glucose units in a cellulose molecule is referred to as the degree of polymerization (DP). Goring and Timell (1962) determined the average DP for native celluloses from several sources using a nitration isolation procedure that minimizes depolymerization and maximizes yield. These molecular weight determinations, done by light-scattering experiments, indicate that wood cellulose has an average DP of at least 9,000–10,000 and possibly as high as 15,000. An average DP of 10,000 would correspond to a linear chain length of approximately 5 μm in wood. This would mean an approximate molecular weight for cellulose ranging from about 10,000 to 150,000. Figure 3.2 shows a partial structure of cellulose.

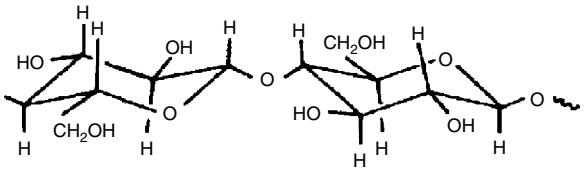

FIGURE 3.1 Chemical structure of cellobiose.

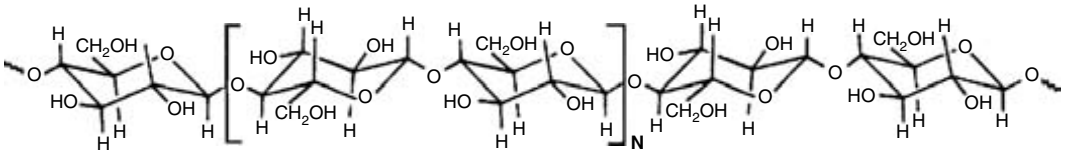

FIGURE 3.2 Partial structure of cellulose.

Cellulose molecules are randomly oriented and have a tendency to form intra- and intermolecular hydrogen bonds. As the packing density of cellulose increases, crystalline regions are formed. Most wood-derived cellulose is highly crystalline and may contain as much as 65% crystalline regions. The remaining portion has a lower packing density and is referred to as amorphous cellulose. X-ray diffraction experiments indicate that crystalline cellulose (*Valonia ventricosa*) has a space group symmetry where a = 16.34 Å and b = 15.72 Å (Figure 3.3, Gardner and Blackwell 1974). The distance of one repeating unit (i.e., one cellobiose unit) is c = 10.38 Å (Figure 3.4). The unit cell contains eight cellobiose moieties. The molecular chains pack in layers that are held together by weak van der Waals forces. The layers consist of parallel chains of anhydroglucopyranose units and the chains are held together by intermolecular hydrogen bonds. There are also intramolecular hydrogen bonds between the atoms of adjacent glucose residues (Figure 3.4). This structure is referred to as cellulose I or native cellulose.

There are several types of cellulose in wood: crystalline and noncrystalline (as described in the preceding paragraph) and accessible and nonaccessible. Accessible and nonaccessible refer to the availability of the cellulose to water, microorganisms, etc. The surfaces of crystalline cellulose are accessible but the rest of the crystalline cellulose is nonaccessible. Most of the noncrystalline cellulose is accessible but part of the noncrystalline cellulose is so covered with both hemicelluloses and lignin that it becomes nonaccessible. Concepts of accessible and nonaccessible cellulose are very important in moisture sorption, pulping, chemical modification, extractions, and interactions with microorganisms.

Cellulose II is another important type of cellulose used for making cellulose derivatives. It is not found in nature. Cellulose II is obtained by mercerization and regeneration of native cellulose. Mercerization is treatment of cellulose I with strong alkali. Regeneration is treatment with carbon disulfide to form a soluble xanthate derivative. The derivative is converted back to cellulose and reprecipitated as cellulose II. Cellulose II has space group a = 8.01 Å, b = 9.04 Å (Figure 3.3), and c = 10.36 Å (Figure 3.4).

There is also a cellulose III structure, which is formed by treatment of cellulose I with liquid ammonia at about –80ºC followed by evaporation of the ammonia. Alkali treatment of cellulose III gives cellulose II. Cellulose IV is formed by heating cellulose III in glycerol at 260ºC.

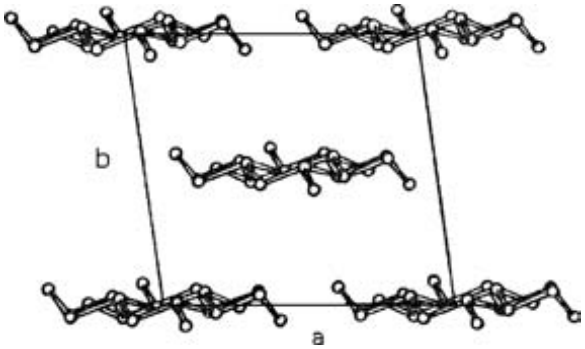

FIGURE 3.3 Axial projection of the crystal structure of cellulose I.

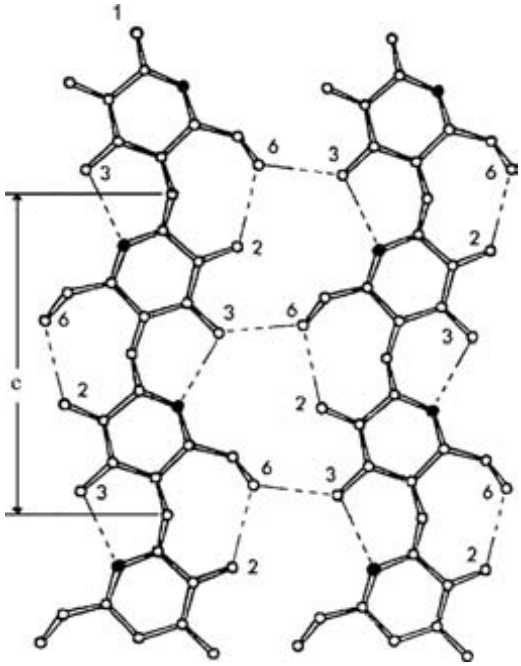

FIGURE 3.4 Planar projection of two cellulose chains showing some of the hydrogen bond between cellulose chains and within a single cellulose chain.

Another type of cellulose (based on the method of extraction from wood) often referred to in the literature is Cross and Bevan cellulose. It consists largely of cellulose I but also contains some hemicellulose. It is obtained by chlorination of wood meal, followed by washing with aqueous solutions of 3% sulfur dioxide (SO_2) and 2% sodium sulfite ($NaSO_3$).

Finally, there is another structure of cellulose referred to as Kürschner cellulose (also based on the method of isolation). Kürschner cellulose is obtained by refluxing wood meal three times for 1 hour with a 1:4 (v/v) mixture of nitric acid and ethyl alcohol. The water-washed and dried cellulose is referred to as Kürschner cellulose, which also contains some hemicelluloses. This method of cellulose isolation is not often used because it destroys some of the cellulose and the nitric acid–ethanol mixture is potentially explosive.

Cellulose I is insoluble in most solvents including strong alkali. Alkali will swell cellulose but not dissolve it. Cellulose dissolves in strong acids such as 72% sulfuric acid, 41% hydrochloric acid, and 85% phosphoric acid, but degradation occurs rapidly. It is difficult to isolate cellulose from wood in a pure form because it is intimately associated with lignin and hemicellulose. The analytical method for isolating cellulose is given in the analytical procedures section of this chapter (Section 3.8).

3.1.3 Hemicelluloses

In general, the hemicellulose fraction of woods consists of a collection of polysaccharide polymers with a lower DP than cellulose (average DP of 100–200) and containing mainly the sugars D-xylopyranose, D-glucopyranose, D-galactopyranose, L-arabinofuranose, D-mannopyranose, D-glucopyranosyluronic acid, and D-galactopyranosyluronic acid with minor amounts of other sugars. The structure of hemicelluloses can be understood by first considering the conformation of the monomer units. There are three entries under each monomer in Figure 3.5. In each entry, the letter designations D and L refer to the standard configurations for the two optical isomers of glyceraldehyde,

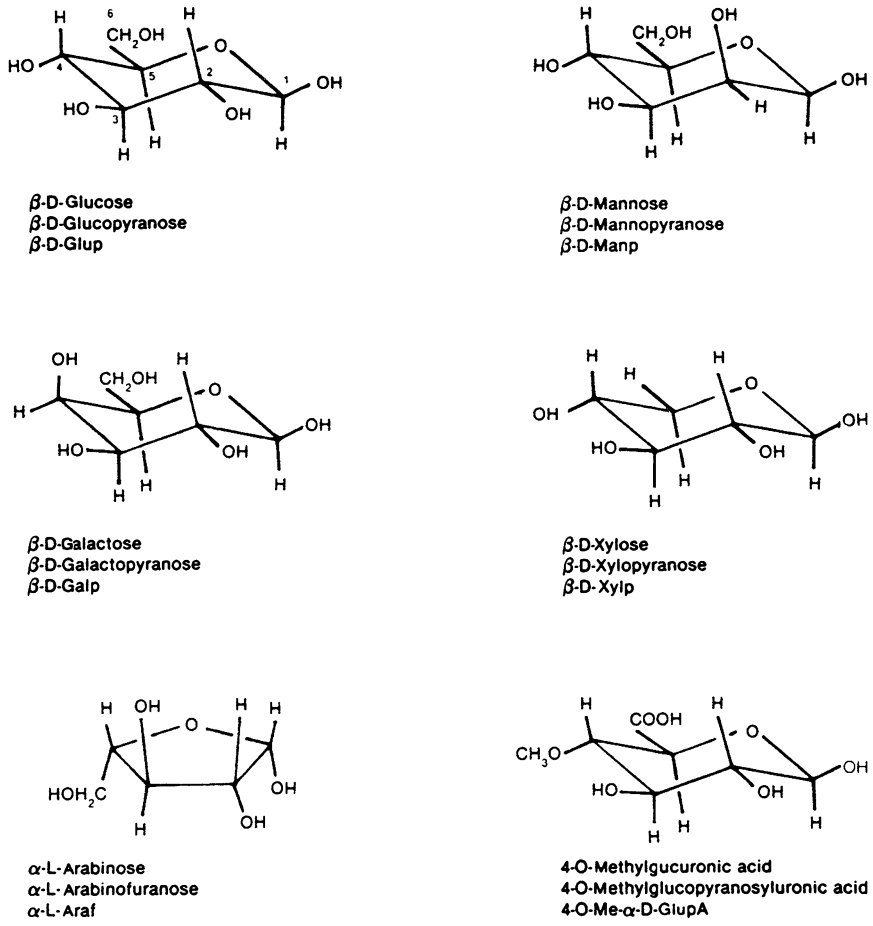

FIGURE 3.5 Sugar monomer components of wood hemicellulose.

the simplest carbohydrate, and designate the conformation of the hydroxyl group at carbon 4 (C-4) for pentoses (xylose and arabinose) and C-5 for hexoses (glucose, galactose, and mannose). The Greek letters α and β refer to the configuration of the hydroxyl group on C-1. The two configurations are called anomers. The first name given for each structure is a shortened form of the sugar name. The second name given for each structure explicitly indicates the ring structure: Furanose refers to a five-membered ring and pyranose refers to a six-membered ring. The six-membered ring is usually in a chair conformation. The third name given for each structure is an abbreviation commonly used for a sugar residue in a polysaccharide (Whistler et al. 1962, Timell 1964, Timell 1965, Whistler and Richards 1970, Jones et al. 1979).

Hemicelluloses are intimately associated with cellulose and contribute to the structural components of the tree. Some hemicelluloses are present in very large amounts when the tree is under stress, e.g., compression wood has a higher D-galactose content as well as a higher lignin content (Timell 1982). They usually contain a backbone consisting of one repeating sugar unit linked β-(1→4) with branch points (1→2), (1→3), and/or (1→6).

Hemicelluloses usually consists of more than one type of sugar unit and are sometimes referred to by the sugars they contain, for example, galactoglucomanan, arabinoglucuronoxylan, arabinogalactan, glucuronoxylan, glucomannan, etc. The hemicelluloses also contain acetyl- and methyl-substituted groups. Hemicelluloses are soluble in alkali and are easily hydrolyzed by acids. A gradient elution at varying alkali concentrations can be used for a crude fractionation of the hemicelluloses from

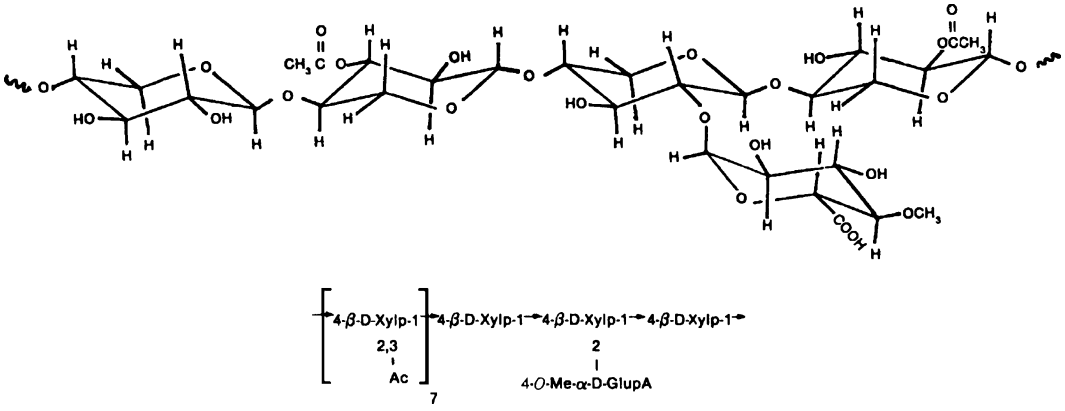

FIGURE 3.6 Partial molecular structure (top) and structure representation (bottom) of *O*-acetyl-4-*O*-methyl-glucuronoxylan.

wood. The hemicelluloses can then be precipitated from the alkaline solution by acidification using acetic acid. Further treatment of the neutralized solution with a neutral organic solvent such as ethyl alcohol results in a more complete precipitation (Sjöström 1981). The detailed structures of most wood hemicelluloses have not been determined. Only the ratios of sugars that these polysaccharides contain have been studied.

3.1.3.1 Hardwood Hemicelluloses

Figure 3.6 shows a partial structure of an *O*-acetyl-4-*O*-methyl-glucuronoxylan from a hardwood. This class of hemicelluloses is usually referred to as glucuronoxylans. This polysaccharide contains a xylan backbone of D-xylopyranose units linked β-(1→4) with acetyl groups at C-2 or C-3 of the xylose units on an average of seven acetyls per ten xylose units (Sjöström 1981). The xylan is substituted with sidechains of 4-*O*-methylglucuronic acid units linked to the xylan backbone α-(1→2) with an average frequency of approximately one uronic acid group per ten xylose units. The sidechains are quite short.

Hardwoods also contain 2–5% of a glucomannan composed of β-D-glucopyranose and β-D-mannopyranose units linked (1→4). The glucose:mannose ratio varies between 1:2 and 1:1 depending on the wood species. Table 3.2 shows the major hemicelluloses found in hardwoods.

TABLE 3.2
Major Hemicelluloses in Hardwoods

Hemicellulose Type DP	Percent in Wood	Units	Molar Ratio	Linkage
Glucuronoxylan 200	15–30	β-D-Xyl*p*	10	1→4
		4-*O*-Me-α-D-Glu*p*A	1 7	1→2
		Acetyl		
Glucomannan 200	2–5	β-D-Man*p*	1-2	1→4
		β-D-Glu*p*	1	1→4

TABLE 3.3
Major Hemicelluloses in Softwoods

Hemicellulose Type DP	Percent in Wood	Units	Molar Ratio	Linkage Avg
Galactoglucomannan 100	5–8	β-D-Man*p*	3	1→4
		β-D-Glu*p*	1	1→4
		α-D-Gal*p*	1	1→6
Galactoglucomannan 100	10–15	β-D-Man*p*	4	1→4
		β-D-Glu*p*	1	1→4
		α-D-Gal*p*	0.1	1→6
		Acetyl	1	
Arabinoglucuronoxylan 100	7–10	β-D-Xyl*p*	10	1→4
		4-*O*-Me-α-D-Glu*p*A	2	1→2
		α-L-Ara*f*	1.3	1→2
Arabinogalactan 200 (Larch wood)	5–35	β-D-Gal*p*	6	1→4
				1→6
		α-L-Ara*f*	2–3	1→6
		β-D-Ara*p*	1–3	1→3
		β-D-Glu*p*A	trace	1→6

3.1.3.2 Softwood Hemicelluloses

Table 3.3 shows the major hemicelluloses from softwoods. One of the main hemicelluloses from softwoods contains a backbone polymer of D-galactose, D-glucose, and D-mannose (Sjöström 1981). The galactoglucomannan is the principal hemicellulose (approximately 20%), with a linear or possibly slightly branched chain with β-(1→4) linkages (Figure 3.7). Glucose and mannose make up the backbone polymer with branches containing galactose. There are two fractions of these polymers, which differ in galactose content. The low-galactose fraction has a ratio of galactose: glucose:mannose of about 0.1:1:4 and the high-galactose fraction has a ratio of 1:1:3. The D-galactopyranose units are linked as a single-unit sidechain by α-(1→6) bonds. The C-2 and C-3 positions of the backbone polymer have acetyl groups substituted on them an average of every three to four hexose units.

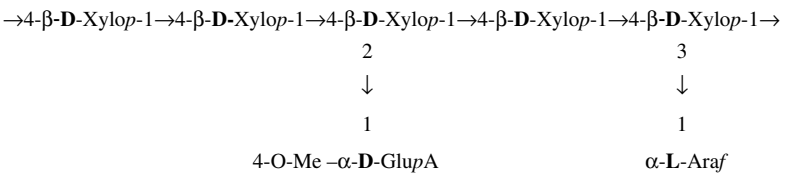

FIGURE 3.7 Partial structure of a softwood arabino 4-*O*-methylglucuronoxylan.

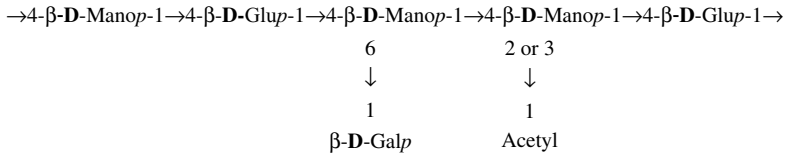

FIGURE 3.8 Partial structure of a softwood *O*-acetyl-galacto-glucomannan.

Another major hemicellulose polymer in softwoods (5–10%) is an arabinoglucuronoxylan consisting of a backbone of β-(1→4) xylopyranose units with α-(1→2) branches of D-glucopyranosyluronic acid on an average of every two to ten xylose units and α-(1→3) branches of L-arabinofuranose, on average, every 1.3 xylose units (Figure 3.8).

Another hemicellulose that is found mainly in the heartwood of larches is an arabinogalactan. Its backbone is a β-(1→3)-linked D-galactopyranose polymer with almost every unit having a branch attached to C-6 of β-D-galactopyranose residues. In some cases this sidechain is β-L-arabinofuranose linked (1→3) or β-D-arabinopyranose linked (16).

There are other minor hemicelluloses in softwoods that mainly contain L-arabinofuranose, D-galactopyranose, D-glucopyranouronic acid, and D-galactopyroanuronic acid (Sjöström 1981).

3.1.4 Other Minor Polysaccharides

Both softwoods and hardwoods contain small amounts of pectins, starch, and proteins. Pectin is a polysaccharide polymer made up of repeating units of D-galacturonic acid linked α-(1→4). Pectin is found in the membranes in the bordered pits between wood cells and in the middle lamella. Degradation of this membrane by microorganisms increases permeability of wood to water-based treatment chemicals such as fire retardants and wood preservatives. Pectins are found in high concentration in the parenchyma cell walls in the inner bark where they may act as a binder. L-Arabinofuranose and D-galactopyranose are often found as a minor part of the pectic substance. Pectin is also found as the methyl ester.

Starch is the principal reserve polysaccharide in plants. Small amount of starch can also be found in the wood cell wall. Starch normally occurs as granules and is composed of D-glucopyranose units linked α-(1→4) (amylose) or α-(1→4) with branches about every 25 glucopyraosyl units at α-(1→6) (amylopectin). Amylose occurs as a helix structure in the solid state due to the α-configuration in the polymer. Amylopectin is highly branched.

3.2 LIGNIN

Lignins are amorphous, highly complex, mainly aromatic polymers of phenylpropane units (Figure 3.9) that are considered to be an encrusting substance. The three-dimensional polymer is made up of C–O–C and C–C linkages. The precursors of lignin biosynthesis are *p*-coumaryl alcohol (Figure 3.9, structure 1), coniferyl alcohol (Figure 3.9, structure 2), and sinapyl alcohol (Figure 3.9, structure 3). Structure 1 is a minor precursor of both softwood and hardwood lignins, structure 2 is the predominate precursor of softwood lignin, and structures 2 and 3 are both precursors of hardwood lignin (Alder 1977).

Softwood lignin has a methoxyl content of 15–16%; hardwood lignin has a methoxyl content of 21%. Lignin does not have a single repeating unit of the hemicelluloses like cellulose does, but instead consists of a complex arrangement of substituted phenolic units.

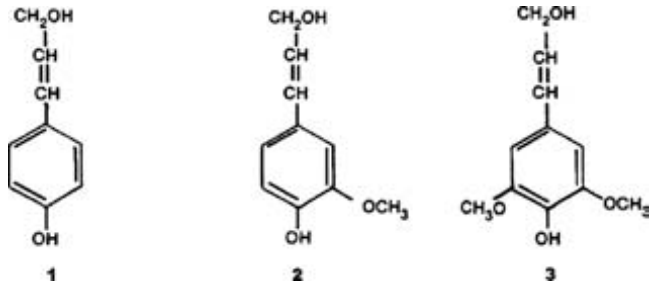

FIGURE 3.9 Chemical structures of lignin precursors: (1) *p*-coumaryl alcohol, (2) coniferyl alcohol, and (3) sinapyl alcohol.

Lignins can be classified in several ways, but they are usually divided according to their structural elements (Sjöström 1981). All wood lignins consist mainly of three basic building blocks of guaiacyl, syringyl, and *p*-hydroxyphenyl moieties, although other aromatic units also exist in many different types of woods. There is a wide variation of structures within different wood species. The lignin content of hardwoods is usually in the range of 18–25%, whereas the lignin content of softwoods varies between 25 and 35%. The phenylpropane can be substituted at the α, β, or γ positions into various combinations linked together both by ether and carbon to carbon linkages (Sakakibara 1991).

Lignins from softwoods are mainly a polymerization product of coniferyl alcohol and are called guaiacyl lignin. Hardwood lignins are mainly syringyl-guauacyl lignin, because they are a copolymer

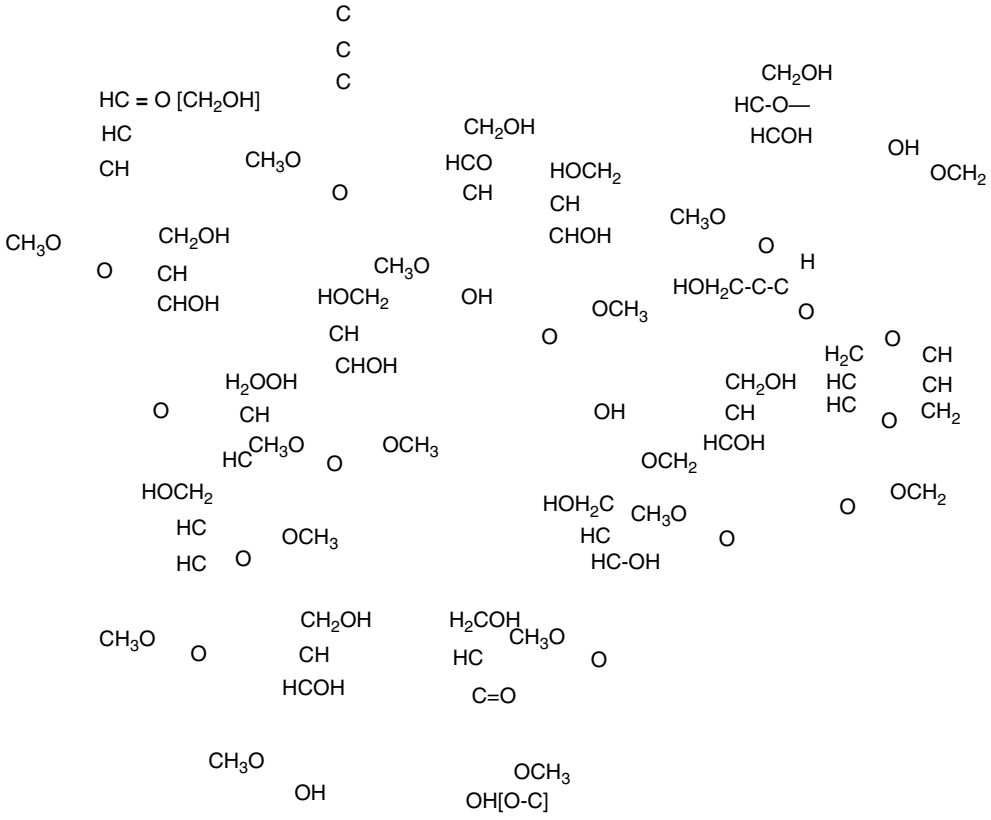

FIGURE 3.10 Partial structure of a softwood lignin.

of coniferyl and sinapyl alcohols. The ratio of these two types varies in different lignins from about 4:1 to 1:2 (Sarkanen and Ludwig 1971). A proposed structure for a hardwood lignin (*Fagus silvatica* L.) is shown in Figure 3.10 (Adler 1977).

Lignins found in woods contain significant amounts of constituents other than guaiacyl- and syringylpropane units (Sarkanen and Ludwig 1971). Lignin is distributed throughout the secondary cell wall, with the highest concentration in the middle lamella. Because of the difference in the volume of middle lamella to secondary cell wall, about 70% of the lignin is located in the cell wall.

Lignin can be isolated from wood in several ways. So-called Klason lignin is obtained after hydrolyzing the polysaccharides with 72% sulfuric acid. It is highly condensed and does not truly represent the lignin in its native state in the wood. The polysaccharides can be removed using enzymes to give an "enzyme lignin" that is much closer to a native lignin than Klason lignin. "Milled wood lignin" or Björkman lignin can be isolated by using a vibratory ball mill on fine wood flour and then extracting with suitable organic solvents (Björkman 1956, 1957). Approximately 30–50% of the native lignin is isolated using this procedure. This procedure is tedious but does isolate a lignin closer to a native lignin.

The molecular weight of lignin depends on the method of extraction. Klason lignin, since it is highly condensed, has molecular weights as low as 260 and as high as 50 million (Goring 1962). Björkman lignin has a molecular weight of approximately 11,000.

Lignins are associated with the hemicelluloses forming, in some cases, lignin–carbohydrate complexes that are resistant to hydrolysis even under pulping conditions (Obst 1982). There is no evidence that lignin is associated with cellulose.

3.3 EXTRACTIVES

As the name implies, extractives (also referred to as natural products) are chemicals in the wood that can be extracted using solvents. In some cases, the extractives are classified by the solvent used to extract them. For example, water-soluble or toluene-ethanol–soluble or ether-soluble extractives. Hundreds of extractives have been identified and in some cases their role in the tree is well understood. In other cases, it is not clear why they are present (Rowe 1989). Extractives, such as pine pitch and resins, have been used for centuries to waterproof wooden boats, in torches, and as a binder. They have also found application in medicine, cosmetics, and as a preservative (Hillis 1989). Some of the extractives in wood are precursors to other chemicals, some are formed in response to wounds, and some act as part of a defense mechanism.

The extractives are a group of cell wall chemicals mainly consisting of fats, fatty acids, fatty alcohols, phenols, terpenes, steroids, resin acids, rosin, waxes, and many other minor organic compounds. These chemicals exist as monomers, dimers, and polymers. In general, softwoods have a higher extractives content than hardwoods. Most of the extractives in both softwoods and hardwoods are located in the heartwood, and some are responsible for the color, smell, and durability of the wood. The qualitative difference in extractive content from species to species is the basis of chemotaxonomy (taxonomy based on chemical constituents).

Resins and fats are made up of resin acids and fatty acids, respectively. Fatty acids are esters with alcohols, such as glycerol, and mainly occur in sapwood. Resin acids have a free carboxylic acid functional group and are mainly found in heartwood (Kai 1991). Abietic acid (Figure 3.11, structure 1) is a common type of resin acid.

The most common terpenes in softwoods are pinene (Figure 3.11, structure 2) and other similar chemical structures. One of the most important polyphenols is pinosylvin (Figure 3.11, structure 3), which is very toxic and found in pine heartwood. Lignans are a combination of two phenylpropane units and are common in softwoods (Gottlieb and Yoshida 1989). Conidendrin (Figure 3.11, structure 4) is found in spruce and hemlock. Tannins in wood can be classified into three classes: gallotannins, ellagtannins, and condensed tannins (Hemingway 1989, Porter 1989). Gallotannins are polymeric esters of gallic acid (Figure 3.11, structure 5) and are usually associated with sugars

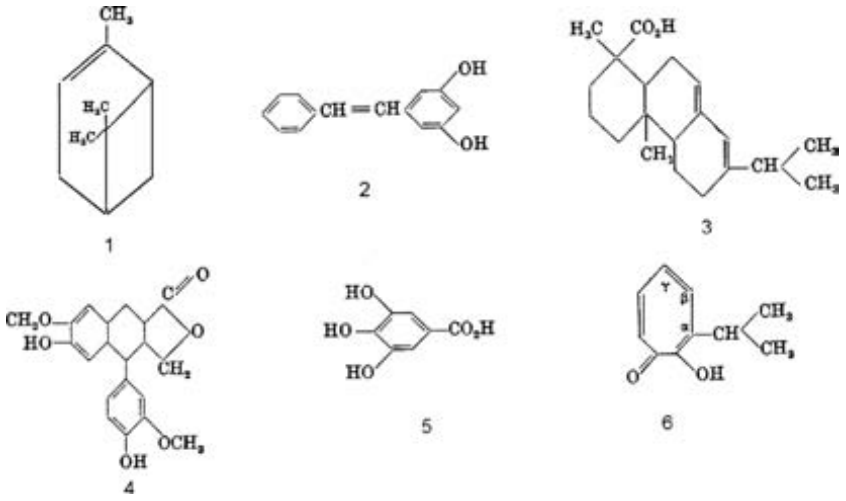

FIGURE 3.11 Chemical structures of some of the extractives in wood: (1) abietic acid, (2) α-pinene, (3) pinosylvin, (4) pineresinol, (5) gallic acid, (6) α-, β-, and γ-thujaplicin.

(Haslam 1989). Tropolones are responsible for the durability of cedar wood. Examples of this class of extractives include α-, β-, and γ-thujaplicin (Figure 3.11, structure 6) (Kollmann and Côté 1968).

3.4 BARK

Bark is a very complex tissue that is composed of two principal zones: the inner bark and the outer bark. The outer bark, which is sometimes referred to as rhytidome and is also known as the periderm, is made up of three layers: the phellem (cork cells), phellogen (cork cambium), and the phelloderm (cork skin). The thickness of the periderm varies greatly between and within species and with the age of the bark. The inner bark, which is referred to as the phloem or bast, is complex in structure and is composed of several types of cells including sieve tubes, fiber cells, albuminose cells, companion cells, parenchyma cells, ideoblasts, and lactifers. Not all cell types occur in every bark. The bark is divided from the wood or xylem by the vascular cambium layer (Sandved et al. 1992).

The chemical composition of bark is complex and varies between and within species, and also between the inner and outer bark. Proximate chemical analysis of bark from different species indicates that the chemical constituents of bark can be classified into four major groups: polysaccharides (cellulose, hemicellulose, and pectic materials); lignin and polyphenols; hydroxy acid complexes (suberin); and extractives (fats, oils, phytosterols, resin acids, waxes, tannins, terpenes, phlobaphenes, and flavonoids). Table 3.4 illustrates the variability of the chemical composition of bark between softwood and hardwood species, *Pinus pinaster* and *Quercus suber,* respectively.

3.4.1 Extractives

The extractives content of bark is quite high compared to wood, but values reported in the literature can be very different even for the same species. These apparent differences depend on the method of extraction. For example, McGinnis and Parikh (1975) reported 19.9% extractives for loblolly pine bark using petroleum ether, benzene, ethanol, and cold and hot water. Labosky (1979) extracted loblolly pine bark with hexane, benzene, ethyl ether, ethanol, water, and 1% sodium hydroxide and reported 27.5% extractives.

The analysis methods developed for wood cannot be used for bark directly. There are many compounds in bark that are not found in wood that interfere with these analysis methods. For example,

TABLE 3.4
Average Chemical Composition of Softwood and Hardwood Bark

Component	Percent Oven-Dry Weight	
	Pinus pinaster[a]	*Quercus suber*[b]
Polysaccharides	41.7 ± 0.9	19.9 ± 2.6
Lignin and polyphenols	43.7 ± 2.4	23.0 ± 0.5
Suberin	1.5 ± 0.2	39.4 ± 1.7
Extractives	11.4 ± 2.2	14.2 ± 1.1
Ash	1.2 ± 0.6	1.2 ± 0.2

[a] Data obtained from Nunes et al. 1996.
[b] Data obtained from Pereira, 1988.

the presence of suberin in bark tends to limit access of delignification reagents to the lignin in the bark, and therefore may lead to a holocellulose that is not pure enough to permit fractionation of individual bark polysaccharides. Suberin, polyflavonoids, and other high-molecular-weight condensed tannins can also complicate analysis of bark lignin, resulting in false high values of lignin content in bark.

Because of the interference of the extractives in polysaccharide and lignin analysis, procedures for elucidation of the chemical composition of bark begin with an extraction protocol that consists of sequential extraction solvents of increasing polarity. A common protocol begins with a diethyl ether extraction step that yields waxes, fatty acids, fats, resin acids, phytosterols, and terpenes. This is followed by an ethyl alcohol extraction step that yields condensed tannins, flavonoids, and phenolics. The third step uses hot water, and yields condensed tannins and water-soluble carbohydrates. To release phenolic acids, hemicelluloses, and suberin monomers from the residue from the third step, 1% aqueous sodium hydroxide is used (Holloway and Deas 1973, Kolattukudy 1984).

The extract fractions from the above-mentioned steps are then subjected to further workup to separate each into easy-to-analyze mixtures of compounds. For example, partitioning the diethyl ether fraction against aqueous sodium bicarbonate separates the fatty acids and resin acids from the neutral components, tannins, terpenes, and flavonoids. The neutral fraction is then saponified to give the alcohols and salts of fatty acids, dicarboxylic, hydroxy-fatty, and ferulic acids. Ethanol extraction followed by hot water extraction of the insoluble ether fraction yields soluble simple sugars and condensed tannins. Sodium hydroxide extraction of the insoluble residue gives soluble suberin monomers, phenolic acids, and hemicelluloses. Sulfuric acid treatment of the insoluble fraction yields lignin (Chang and Mitchell 1955, Hemingway 1981, Laks 1991).

3.4.1.1 Chemical Composition of Extractives

The waxes in bark are esters of high-molecular-weight long-chain monohydroxy-alcohol fatty acids. A lot of research has been done on softwood waxes, but very little on hardwood waxes. At one time, hardwood waxes were produced commercially for use in polishes, lubricants, additives to concrete, carbon paper, fertilizers, and fruit coatings (Hemingway 1981).

Terpenes are a condensation of two or more five-carbon isoprene (2-methy-1,3-butadiene) units in a linear or cyclic structure. They can also contain various functional groups. The most common of the monoterpenes are α- and β-pinenes found in firs and pines. Birch bark can contain up to 25% terpenes, by total dry weight (Seshadri and Vedantham 1971).

Flavonoids are a group of compounds based on a 15-carbon hydroxylated tricyclic unit (Laks 1991). They are often found as glycosides. Many tree barks are rich in mono- and polyflavonoids (Hergert 1960, 1962). Their function seems to be as an antioxidant, pigment, and growth regulator (Laks 1991).

Hydrolyzable and condensed tannins are also major extractives from bark. The hydrolyzable tannins are esters of carboxylic acids and sugars that are easily hydrolyzed to give benzoic acid derivatives and sugars. Over 20 different hydrolyzable tannins have been isolated from oaks (Nonaka et al. 1985).

The condensed tannins are a group of polymers based on a hydroxylated C-15 flavonoid monomer unit. Low degree of polymerization tannins are soluble in polar solvents, whereas the high degree of polymerization tannins are soluble in dilute alkali solutions (Hemingway et al. 1983). It is difficult to isolate pure fractions of tannins and the structure can be altered by the extraction procedure.

Free sugars are also extracted from bark. Hot water extraction yields about 5% free sugar fraction, which is mainly composed of glucose and fructose; this amount varies depending on the growing season. For example, the free sugar content is low in early spring and increases during the growing season, reaching a maximum in the fall (Laks 1991). Other minor free sugars found in bark include galactose, xylose, mannose, and sucrose. Hydrolysis of the hot water extract of bark yields more free sugars, the most abundant one being arabinose. These sugars are tied up as glycosides or in the hemicelluloses. Other sugars released during hydrolysis are glucose, fructose, galactose, xylose, mannose, and rhamnose.

3.4.2 Hemicelluloses

The hemicellulose content of different barks varies from 9.3% for *Quercus robur* to 23.1% for *Fagus sylvatica* (Dietrichs et al. 1978). The main hemicellulose in conifer barks is a galactoglucomannan. Arabino-4-*O*-methyl-glucuronoxylan is the main hemicellulose in deciduous barks. In general, bark xylans and glucomannans are similar to ones found in wood. Other hemicelluloses that have been isolated from barks include 4-*O*-methy-glucuronoxylans, glucomannans, *O*-acetyl-galactoglucomannan, and *O*-acetyl-4-*O*-methyl-glucuronoxylan (Painter and Purves 1960, Jiang and Timell 1972, Dietrichs 1975). In the xylans, the xylose units are connected β-(1$\rightarrow$4) and the glucuronic acid groups are attached to the xylan backbone α-(1$\rightarrow$2). The ratio of xylose to GluU is 10:1 with a degree of polymerization of between 171 and 234 (Mian and Timell 1960). Glucomannans from deciduous barks contain mannose and glucose units in a ratio of from 1:1 to 1.4:1 (Timell 1982). In the mannans from the barks of aspen and willow, galactose units were found as sidechains. The ratio of mannose: glucose:galactose was 1.3:1:0.5 with an average degree of polymerization of 30 to 50 (Timell 1982).

Arabinans have been reported in the barks of aspen, spruce, and pine (Painter and Purves 1960). The backbone is α-(1$\rightarrow$5)-arabinofuranose units and, in the case of pine, the average degree of polymerization is 95 (Timell 1982). A group of galacturonic acid polymers has been isolated from birch. One is a galacturonic acid backbone linked α-(1$\rightarrow$4) with arabinose sidechains in a ratio of galacturonic acid to arabinose of 9:1, and another consists of galacturonic acid, arabinose, and galactose in a ratio of 7:3:1. Small amounts of glucose, xylose, and rhamnose were also found in these polymers (Mian and Timell 1960, Timell 1982).

A pectic substance that contains either galactose alone or galactose and arabinose units has also been isolated from barks (Toman et al. 1976). The pure galactan is water-soluble and consists of 33 β-(1$\rightarrow$4)-linked galactose units with a sidechain at C-6 of the backbone. A highly branched arabinogalactan was found in the bark of spruce with a ratio of galactose to arabinose of 10:1 (Painter and Purves 1960).

In almost all cases, the hemicelluloses found in bark are similar to those found in wood, with some variations in composition. Table 3.5 shows the sugars present after hydrolysis of the polysaccharides in bark.

TABLE 3.5
Sugars Present in Hydrolyzates of Some Tree Barks

Species	Glu	Man	Gal	Xyl	Ara	Rha	UrA	Ac
Abies amabills	37.4	8.0	1.6	3.2	3.2	—	5.6	0.8
Picea abies	36.6	6.5	1.3	4.8	1.8	0.3	—	—
Picea engelmannii	35.7	2.9	2.4	3.8	3.3	—	8.0	0.5
Pinus contoria								
Inner bark	40.9	2.5	4.3	3.7	10.6	—	9.9	0.2
Outer bark	26.8	2.5	4.2	3.4	5.5	—	7.7	0.8
Pinus sylvestris	30.2	5.4	2.4	5.8	2.1	0.3	—	—
Pinus taeda								
Inner bark	21.3	2.5	3.1	2.1	5.6	0.3	4.6	—
Outer bark	15.8	2.6	2.5	3.8	1.8	0.1	2.1	—
Betula papyrifera								
Inner bark	28.0	0.2	1.0	21.0	2.7	—	2.2	—
Fagus sylvatica	29.7	0.2	3.1	20.1	3.1	1.2	—	—
Quercus robur	32.3	0.5	1.3	16.4	2.0	0.5	—	—

Source: Fengel and Wegener, 1984.

3.4.3 Cellulose

The cellulose content of barks ranges from 16–41% depending on the method of extraction. In unextracted bark, the cellulose content was between 20.2% for pine and 32.6% for oak (Dietrichs et al. 1978). The high extractives content, especially of suberin, requires harsh conditions to isolate the cellulose, so the cellulose content is usually low and the cellulose is degraded during the isolation process. The outer bark usually contains less cellulose than the inner bark (Harun and Labosky 1985).

Timell (1961a,b) and Mian and Timell (1960), found a number average degree of polymerization for bark cellulose of 125 (*Betula papyrifera*) to 700 (*Pinus contorta*), and a weight average of 4000 (*Abies amabilis, Populus grandidentata*) to 6900 (*Pinus contorta*). Bark cellulose has the same type of crystalline lattice (cellulose I) as normal wood, but the degree of crystallinity is less.

3.4.4 Lignin

As with other analyses involving bark components, literature values for lignin content can vary depending on the method of extraction (Kurth and Smith 1954, Higuchi et al. 1967). Bark contains high contents of condensed and hydrolyzable tannins and sulfuric acid-insoluble suberin that can give false high values of lignin content. For example, the Klason lignin from *Pinus taeda* bark is 46.0% when including both lignin and condensed tannins but only 20.4% when the bark is first extracted with alkali (McGinnis and Parikh 1975). Other researchers have found lignin contents from 38–58% (Labosky 1979). The elemental composition and functional group content of bark lignins are similar to those of the lignin from the wood of the same species (Sarkanen and Hergert 1971, Hemingway 1981). There is less lignin in the inner bark as compared to the outer bark.

There is a lower ratio of OCH_3 groups in aspen bark than in aspen wood and a higher ratio of phenolic OH groups to OCH_3 (Clermont 1970). There are more guaiacyl units in deciduous bark and more *p*-hydroxyphenyl units in coniferous bark as compared to the wood of the same species (Andersson et al. 1973). While there are some differences in the ratios of components, no structural difference have been found between most bark lignins and the corresponding wood.

3.4.5 Inorganics and pH

Bark is generally higher in inorganics than normal wood. The inorganic (ash) content can be as high as 13% and, in general, the inner bark contains more inorganics as compared to the outer bark (Young 1971, Choong et al. 1976, Hattula and Johanson 1978, Harper and Einspahr 1980). For example, the outer bark of willow contains 11.5% ash, the inner bark 13.1%, and the sapwood 0.9%; sweetgum outer bark is 10.4%, inner bark 12.8%, and sapwood 0.5% ash; red oak outer bark is 8.9%, inner bark 11.1%, and sapwood 0.9% ash; and ash outer bark is 12.3%, inner bark 12.1%, and sapwood 0.9% ash. The major inorganic elements in bark are Na, K, Ca, Mg, Mn, Zn, and P (Choong et al. 1976). There is more Na, K, Mg, Mn, Zn, and P in sapwood than in bark and more Ca in bark than in sapwood.

In general, the pH of bark is lower than that of the corresponding wood due to the higher inorganic content of bark compared to wood. For example, Martin and Gray (1971) reported pH values of southern pines ranging from about 3.1–3.8 with an average of 3.4–3.5 compared to a pH of 4.4–4.6 for sapwood. The outer bark has a lower pH than the inner bark, presumably due to a higher content of Ca in the outer bark (Volz 1971). The pH of bark decreases slightly with the age of the tree.

3.5 INORGANICS

The inorganic content of a wood is usually referred to as its ash content, which is an approximate measure of the mineral salts and other inorganic matter in the fiber after combustion at a temperature of 575 ± 25°C. The inorganic content can be quite high in woods containing large amounts of silica; however, in most cases, the inorganic content is less than 0.5% (Browning 1967). This small amount of inorganic material contains a wide variety of elements (Ellis 1965, Young and Guinn 1966). Ca, Mg, and K make up 80% of the ash in wood. These elements probably exist in the wood as oxalates, carbonates, and sulfates, or bound to carboxyl groups in pectic materials (Hon and Shiraishi 1991). Other elements present are Na, Si, B, Mn, Fe, Mo, Cu, Zn, Ag, Al, Ba, Co, Cr, Ni, Pb, Rb, Sr, Ti, Au, Ga, In, La, Li, Sn, V, and Zr (Ellis 1965). Some of these are essential for wood growth. Inorganic ions are absorbed into the tree through the roots and transported throughout the tree. Young and Guinn (1966) determined the distribution of 12 inorganic elements in various part of a tree (roots, bark, wood, and leaves) and concluded that both the total inorganic content and concentration of each element varied widely both within and between species. The inorganic content varies depending on the environmental conditions in which the tree lives. See Table 3.12 for a partial list of the inorganic content of some woods.

Saka and Goring (1983) studied the distribution of inorganics from the pith to the outer ring of black spruce (*Picea mariana* Mill) using EDXA. They found 15 different elements including Na, Mg, Al, S, K, Ca, Fe, Ni, Cu, Zn, and Pb. They also found that the inorganic content was higher in earlywood as compared to latewood.

The pH of wood varies from 4.2 (*Pinus sylvestris*) to 5.3 (*Fagus sylvatica*) with an average of approximately 4.7.

3.6 DISTRIBUTION OF CHEMICAL COMPONENTS IN THE CELL WALL

The content of cell wall components depends on the tree species and where in the tree the sample is taken. Softwoods are different from hardwoods, heartwood from sapwood, and latewood from earlywood. Table 3.6 shows the cell wall polysaccharides in earlywood compared to latewood (Saka 1991). Latewood contains more glucomannans as compared to earlywood, but earlywood contains more glucuronoarabinoxylans. Heartwood contains more extractives than sapwood, and as sapwood is transformed into heartwood, aspiration of the bordered pits takes place in softwoods

TABLE 3.6
Cell Wall Polysaccharides in Earlywood and Latewood in Pine

Cell Wall Component	Earlywood%	Latewood%
Cellulose	56.7	56.2
Galactan	3.4	3.1
Glucomannan	20.3	24.8
Arabinan	1.0	1.8
Glucuronoarabinoxylan	18.6	14.1

Source: Saka, 1991.

and encrustation of pit membranes with the formation of tyloses occurs in hardwoods. Earlywood contains more lignin than latewood.

Figure 3.12 shows the distribution of components across the cell wall of scotch pine. The middle lamella and primary wall is mainly composed of lignin (84%) with lesser amounts of hemicelluloses (13.3%) and even less cellulose (07%). The S_1 layer is composed of 51.7% lignin, 30.0% cellulose, and 18.3% hemicelluloses. The S_2 layer is composed of 15.1% lignin, 54.3% cellulose, and 30.6% hemicelluloses. The S_3 layer has little or no lignin, 13% cellulose, and 87% hemicelluloses. The content of xylan is lowest in the S_2 layer and higher in the S_1 and S_3 layers. The concentration of galactoglucomannan is higher in the S_2 than in the S_1 or S_3 layers. On a percentage basis, the middle lamella and primary wall contain the highest concentration of lignin but there is more lignin in the S_2 because it is a much thicker layer as compared to the middle lamella and primary wall. The lignin in the S_2 layer is evenly distributed throughout the layer.

The angle of the cellulose microfibrils in the various cell wall layers, in relation to the fiber axis, is known as the fibril angle. It is one of the most important structural parameters determining mechanical properties of wood. For normal wood, the microfibril angle of the cellulose in the S_2

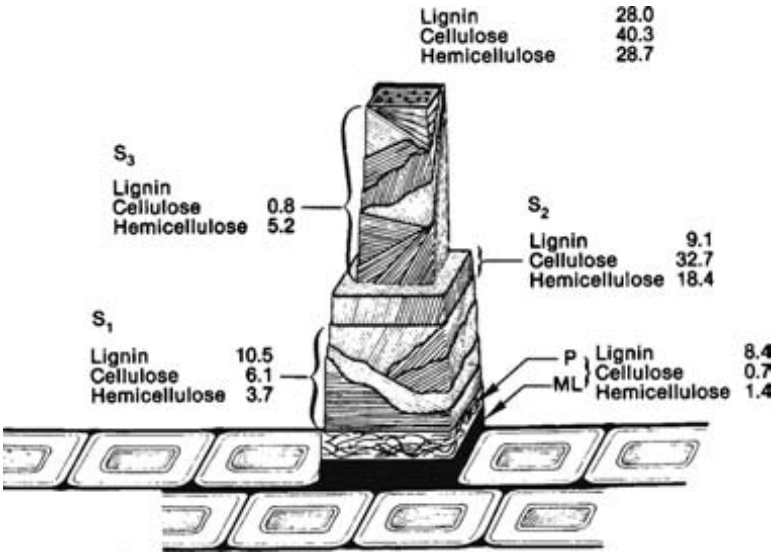

FIGURE 3.12 Chemical composition of the cell wall of scots pine.

layer is 14–19 degrees. It is because this angle is so low in the thick S_2 layer that wood does not swell or shrink to as large an extent in the longitudinal direction (0.1–0.3%).

A further discussion of the distribution of the hemicelluloses in the cell wall can be found in Chapter 15. Strength properties of wood are related to the distribution of hemicelluloses in the cell wall.

3.7 JUVENILE WOOD AND REACTION WOOD

Juvenile wood is the wood that develops in the early stages of tree growth. It physical properties are described in Chapter 2 part 13. Juvenile wood cells are shorter, have smaller cell diameter, larger microfibril angle (up to 55 degrees) and have a high content of compression wood as compared to mature wood. Juvenile wood has a lower density and strength than mature wood. Juvenile wood has less cellulose, more hemicelluloses and lignin compared to mature wood. There is a gradual increase in cellulose content as the cells mature and a gradual decrease in hemicellulose content. The lignin content decreases more rapidly as the cell mature.

Normal wood growth is erect and vertical. When a tree is forced out of this pattern either by wind or gravitational forces, abnormal woody tissue is formed in different parts of the tree to compensate for the abnormal growing conditions. The wood cells that are formed when softwoods and hardwoods are out of vertical are called reaction wood since these cells are reacting to the stressful conditions. In softwoods, irregular cells develop on the underside of a stem or branch and are referred to as compression wood. In hardwoods, irregular cells develop on the upper side of a stem or branch and are referred to as tension wood.

Table 3.7 shows the chemical composition of softwood compression wood (Panshin and de Zeeuw 1980, Timell 1982). Compression wood has a higher lignin content and a lower cellulose content as compared to normal wood. The cellulose in the S_2 layer has a lower degree of crystallization than normal wood and the lignin is largely concentrated in the S_2 layer as compared to normal wood. Forty percent of the lignin is is in the outer zone of the S_2 layer and an additional 40% is uniformly distributed over the remaining part of the S_2 layer (Panshin and de Zeeuw 1980). There are more galactoglucomannans in normal wood and more $1 \rightarrow 3$ linked glucans and galactans in compression wood. The midrofibril angle in the modified S_2 layer in compression wood is quite high (44–47°) and have more rounded tracheids that are 10 to 40% shorter than normal tracheids. Compression wood is weaker than normal wood and lower elastic properties. The reduced cellulose content and high microfibril angle is probably responsible for the reduction in mechanical properties (Panshin and de Zeeuw 1980).

TABLE 3.7
Chemical Composition of Compression Wood in Softwoods

Cell Wall Component	Normal Wood		Compression Wood	
	Range%	Average%	Range%	Average%
Lignin	24.2–33.3	28.8	30.9–40.9	37.7
Cellulose	37.7–60.6	44.6	27.3–53.7	34.9
Galactoglucomannan	—	18	—	9
1,3-Glucan	—	Trace	—	2
Galactan	1.0–3.8	2.2	7.1–12.9	10.0
Glucuronoarabinoxylan	—	8	—	8
Other polysaccharides	—	2	—	2

Data from Panshin and Zeeuw, 1980, and Timell, 1982.

TABLE 3.8
Chemical Composition of Tension Wood in Hardwoods

Cell Wall Component	Normal Wood	Compression Wood
Lignin	29%	14%
Cellulose	44%	57%
Pentosans	15%	11%
Acetyl	3%	2%
Galactosans	2%	7%

Source: Schwerin, 1958.

Table 3.8 shows the chemical composition of hardwood tension wood (Schwerin 1958). Tension wood has a lower lignin content and a higher cellulose content as compared to normal wood. There is a lower content of pentosans (xylans) and acetyls than in normal wood and more galactosans in tension wood. There is no S_3 layer in tension wood but rather what is known as a G layer or gelatinous layer. This layer is approximately 98% cellulose. The cellulose in the G layer is highly crystalline with a microfibril angle of only 5% and contains very little hemicelluloses or lignin. The G layer is as thick or thicker than the S_2 layer in normal wood and contains about the same quantity of inorganics. Tension wood has lower mechanical properties as compared to normal wood (Panshin and de Zeeuw 1980). For example, compression parallel and perpendicular to the grain, modulus of elasticity in bending, modulus of rupture in static bending and longitudinal shear are all reduced in tension wood as compared to normal wood.

3.8 ANALYTICAL PROCEDURES

Chemical composition varies from species to species and within different parts of the same wood species. Chemical composition also varies within woods from different geographic locations, ages, climates and soil conditions.

There are hundreds of reports on the chemical composition of wood material. In reviewing this vast amount of data, it becomes apparent that the analytical procedures used, in many cases, are different from lab to lab and a complete description of what procedure was used in the analysis is not clear. For example, many descriptions do not describe if the samples were pre-extracted with some solvent before analysis. Others do not follow a published procedure so comparison of data is not possible. The following section is composed of standard procedures used in many laboratories to determine the chemical components of the wood cell wall. Tables 3.9 through 3.12 give summaries of various types of chemical compositions of hardwoods and softwoods in the United States. This data has been collected from the analytical laboratories of the USDA, Forest Service, Forest Products Laboratory from 1927 to 1968.

3.8.1 Sampling Procedure

In reporting the chemical content of a wood, it is very important to report as much information about the samples as possible. Since the chemical content of a given species may vary depending upon the growing conditions, harvesting times of the year, etc., it is critical to report these conditions along with the chemical analysis. It is also important to report the exact analytical conditions and procedures used. This way, it may be possible to reproduce the results by other workers in different laboratories. Without this information, it is not possible to compare data from different laboratories.

TABLE 3.9
Methoxyl Content of Some Common Hardwoods and Softwoods

Type of Wood	Methoxy Content (%)
Hardwoods	
Balsa	5.68
Basswood	6.00
Yellow birch	6.07
Shellbark hickory	5.63
Sugar maple	7.25
Mesquite	5.55
Tanoak	5.74
Softwoods	
Incense cedar	6.24
Alaska cedar	5.25
Douglas fir	4.95
Western larch	5.03
Longleaf pine	5.05
Western white pine	4.56
Redwood	5.21
White spruce	5.30

Source: Moore and Johnson, 1967.

The following information should accompany each chemical analysis:

1. Source of the wood
   a. Geographic location
   b. Part of the tree sampled
   c. Date sample was taken
2. Sampling
   a. Different anatomical parts
   b. Degree of biological deterioration, if any
   c. Sample size
   d. Drying method applied
3. Analytical procedure used
4. Calculations and reporting technique

All of the above-mentioned criteria could contribute in one way or another toward variations in chemical analyses.

3.8.2 Extraction

3.8.2.1 Scope and Summary

This method describes a procedure for extraction of wood for further analysis, such as holocellulose, hemicellulose, cellulose, and lignin analysis.

$$\text{Wood materials} = \text{Extractives} + \text{holocellulose} + \text{lignin} + \text{inorganics (ash)}$$

TABLE 3.10
Acetyl Content of Some Common Hardwoods and Softwoods

Type of Wood	Acetyl Content (%)
Hardwoods	
Aspen	3.4
Balsa	4.2
Basswood	4.2
Beech	3.9
Yellow birch	3.3
White birch	3.1
Paper birch	4.4
American elm	3.9
Shellbark hickory	1.8
Red maple	3.8
Sugar maple	3.2
Mesquite	1.5
Overcup oak	2.8
Southern red oak	3.3
Tanoak	3.8
Softwoods	
Eastern white-cedar	1.1
Incense-cedar	0.7
Western red-cedar	0.5
Alaska-cedar	1.1
Douglas-fir	0.7
Balsam fir	1.5
Eastern hemlock	1.7
Western hemlock	1.2
Western larch	0.5
Jack pine	1.2
Loblolly pine	1.1
Longleaf pine	0.6
Western white pine	0.7
Redwood	0.8
White spruce	1.3
Tamarack	1.5

Source: Moore and Johnson, 1967.

Neutral solvents, water, toluene or ethanol, or combinations of solvents are employed to remove extractives in wood. However, other solvents ranging from diethyl ether to 1% NaOH, etc. could be applied according to the nature of extractives and sample type, i.e., bark, leaves, etc.

3.8.2.2 Sample Preparation

It is highly recommended to have a fresh sample. If this is not possible, keep the sample frozen or in a refrigerator to avoid fungal attack. Peel off the bark from the stem and separate the sample into component parts. Dry samples are oven dried for 24 hours (usually at 105ºC) prior to milling. Wet samples can be milled while frozen in order to prevent oxidation or other undesirable chemical reactions. Samples are ground to pass 40 mesh (0.40 mm) using a Wiley Mill.

TABLE 3.11
Chemical Composition of North American Hardwoods and Softwoods

Botanical Name	Common Name	Holo Cellulose	Alpha Cellulose	Pentosans	Klason Lignin	Solubility				
						1% NaOH	Hot Water	EtOH/ Benzene	Ether	Ash
Hardwoods										
Acer macrophyllum	Bigleaf maple	—	46.0	22.0	25.0	18.0	2.0	3.0	0.7	0.5
Acer negundo	Boxelder	—	45.0	20.0	30.0	10.0	—	—	0.4	—
Acer rubrum	Red maple	77.0	47.0	18.0	21.0	16.0	3.0	2.0	0.7	0.4
Acer saccharinum	Silver maple	—	42.0	19.0	21.0	21.0	4.0	3.0	0.6	—
Acer saccharum	Sugar maple	—	45.0	17.0	22.0	15.0	3.0	3.0	0.5	0.2
Alnus rubra	Red alder	74.0	44.0	20.0	24.0	16.0	3.0	2.0	0.5	0.3
Arbutus menziesii	Pacific madrone	—	44.0	23.0	21.0	23.0	5.0	7.0	0.4	0.7
Betula alleghaniensis	Yellow birch	73.0	47.0	23.0	21.0	16.0	2.0	2.0	1.2	0.7
Betula nigra	River birch	—	41.0	23.0	21.0	21.0	4.0	2.0	0.5	—
Betula papyrifera	Paper birch	78.0	45.0	23.0	18.0	17.0	2.0	3.0	1.4	0.3
Carya cordiformus	Bitternut hickory	—	44.0	19.0	25.0	16.0	5.0	4.0	0.5	—
Carya glaubra	Pignut hickory	71.0	49.0	17.0	24.0	17.0	5.0	4.0	0.4	0.8
Carya ovata	Shagbark hickory	71.0	48.0	18.0	21.0	18.0	5.0	3.0	0.4	0.6
Carya pallida	Sand hickory	69.0	50.0	17.0	23.0	18.0	7.0	4.0	0.4	1.0
Carya tomentosa	Mockernut hickory	71.0	48.0	18.0	21.0	17.0	5.0	4.0	0.4	0.6
Celtis laevigata	Sugarberry	—	40.0	22.0	21.0	23.0	6.0	3.0	0.3	—
Eucalyptus gigantea	Alpine ash	72.0	49.0	14.0	22.0	16.0	7.0	4.0	0.3	0.2
Fagus grandifolia	American beech	77.0	49.0	20.0	22.0	14.0	2.0	2.0	0.8	0.4
Fraxinus americana	White ash	—	41.0	15.0	26.0	16.0	7.0	5.0	0.5	—
Fraxinus pennsylvanica	Green ash	—	40.0	18.0	26.0	19.0	7.0	5.0	0.4	—
Gleditsia triacanthos	Honey locust	—	52.0	22.0	21.0	19.0	—	—	0.4	—
Laguncularia racemosa	White mangrove	—	40.0	19.0	23.0	29.0	15.0	6.0	2.1	—
Liquidambar styraciflua	Sweetgum	—	46.0	20.0	21.0	15.0	3.0	2.0	0.7	0.3
Liriodendron tulipifera	Yellow poplar	—	45.0	19.0	20.0	17.0	2.0	1.0	0.2	1.0

Lithocarpus densiflorus	Tanoak	71.0	46.0	20.0	19.0	20.0	5.0	3.0	0.4	0.7
Milalenca quinquenervia	Cajeput	—	43.0	19.0	27.0	21.0	4.0	2.0	0.5	—
Nyssa aquatica	Water tupelo	—	45.0	16.0	24.0	16.0	4.0	3.0	0.6	0.6
Nyssa sylvatica	Black tupelo	72.0	45.0	17.0	27.0	15.0	3.0	2.0	0.4	0.5
Populus alba	White poplar	—	52.0	23.0	16.0	20.0	4.0	5.0	0.9	—
Populus deletoides	Eastern cottonwood	—	47.0	18.0	23.0	15.0	2.0	2.0	0.8	0.4
Populus tremoides	Quaking aspen	78.0	49.0	19.0	19.0	18.0	3.0	3.0	1.2	0.4
Populus trichocarpa	Black cottonwood	—	49.0	19.0	21.0	18.0	3.0	3.0	0.7	0.5
Prunus serotina	Black cherry	85.0	45.0	20.0	21.0	18.0	4.0	5.0	0.9	0.1
Quercus alba	White oak	67.0	47.0	20.0	27.0	19.0	6.0	3.0	0.5	0.4
Quercus coccinea	Scarlet oak	63.0	46.0	18.0	28.0	20.0	6.0	3.0	0.4	—
Quercus douglasii	Blue oak	59.0	40.0	22.0	27.0	23.0	11.0	5.0	1.4	1.4
Quercus falcata	Southern red oak	69.0	42.0	20.0	25.0	17.0	6.0	4.0	0.3	0.4
Quercus kelloggii	California black oak	60.0	37.0	23.0	26.0	26.0	10.0	5.0	1.5	0.4
Quercus lobata	Valley oak	70.0	43.0	19.0	19.0	23.0	5.0	7.0	1.0	0.9
Quercus lyrata	Overcup oak	—	40.0	18.0	28.0	24.0	9.0	5.0	1.2	0.3
Quercus marylandica	Blackjack oak	—	44.0	20.0	26.0	15.0	5.0	4.0	0.6	—
Quercus prinus	Chestnut oak	76.0	47.0	19.0	24.0	21.0	7.0	5.0	0.6	0.4
Quercus rubra	Northern red oak	69.0	46.0	22.0	24.0	22.0	6.0	5.0	1.2	0.4
Quercus stellata	Post oak	—	41.0	18.0	24.0	21.0	8.0	4.0	0.5	1.2
Quercus velutina	Black oak	71.0	48.0	20.0	24.0	18.0	6.0	5.0	0.2	0.2
Salix nigra	Black willow	—	46.0	19.0	21.0	19.0	4.0	2.0	0.6	—
Tilia heterophylla	Basswood	77.0	48.0	17.0	20.0	20.0	2.0	4.0	2.1	0.7
Ulmus americana	American elm	73.0	50.0	17.0	22.0	16.0	3.0	2.0	0.5	0.4
Ulmus crassifolia	Cedar elm	—	50.0	19.0	27.0	14.0	—	—	0.3	—

(*Continued*)

TABLE 3.11
Chemical Composition of North American Hardwoods and Softwoods (*Continued*)

Botanical Name	Common Name	Holo Cellulose	Alpha Cellulose	Pentosans	Klason Lignin	Solubility				
						1% NaOH	Hot Water	EtOH/ Benzene	Ether	Ash
Softwoods										
Abies amabilis	Pacific silver fir	—	44.0	10.0	29.0	11.0	3.0	3.0	0.7	0.4
Abies balsamea	Balsam fir	—	42.0	11.0	29.0	11.0	4.0	3.0	1.0	0.4
Abies concolor	White fir	66.0	49.0	6.0	28.0	13.0	5.0	2.0	0.3	0.4
Abies lasiocarpa	Subalpine fir	67.0	46.0	9.0	29.0	12.0	3.0	3.0	0.6	0.5
Abies procera	Noble fir	61.0	43.0	9.0	29.0	10.0	2.0	3.0	0.6	0.4
Chamaecyparis thyoides	Atlantic white cedar	—	41.0	9.0	33.0	16.0	3.0	6.0	2.4	—
Juniperus deppeana	Alligator juniper	57.0	40.0	5.0	34.0	16.0	3.0	7.0	2.4	0.3
Larix larcina	Tamarack	64.0	44.0	8.0	26.0	14.0	7.0	3.0	0.9	0.3
Larix occidentalis	Western larch	65.0	48.0	9.0	27.0	16.0	6.0	2.0	0.8	0.4
Libocedrus decurrens	Incense cedar	56.0	37.0	12.0	34.0	9.0	3.0	3.0	0.8	0.3
Picea engelmanni	Engelman spruce	69.0	45.0	10.0	28.0	11.0	2.0	2.0	1.1	0.2
Picea glauca	White spruce	—	43.0	13.0	29.0	12.0	3.0	2.0	1.1	0.3
Picea mariana	Black spruce	—	43.0	12.0	27.0	11.0	3.0	2.0	1.0	0.3
Picea sitchensis	Sitka spruce	—	45.0	7.0	27.0	12.0	4.0	4.0	0.7	—
Pinus attenuata	Knobcone pine	—	47.0	14.0	27.0	11.0	3.0	1.0	—	0.2
Pinus banksiana	Jack pine	66.0	43.0	13.0	27.0	13.0	3.0	5.0	3.0	0.3
Pinus clausa	Sand pine	—	44.0	11.0	27.0	12.0	2.0	3.0	1.0	0.4
Pinus contorta	Lodgepole pine	68.0	45.0	10.0	26.0	13.0	4.0	3.0	1.6	0.3
Pinus echinata	Shortleaf pine	69.0	45.0	12.0	28.0	12.0	2.0	4.0	2.9	0.4
Pinus elliottii	Slash pine	64.0	46.0	11.0	27.0	13.0	3.0	4.0	3.3	0.2
Pinus monticola	Western white pine	69.0	43.0	9.0	25.0	13.0	4.0	4.0	2.3	0.2

Pinus palustris	Longleaf pine	—	44.0	12.0	30.0	12.0	3.0	4.0	1.4	—
Pinus ponderosa	Ponderosa pine	68.0	41.0	9.0	26.0	16.0	4.0	5.0	5.5	0.5
Pinus resinosa	Red pine	71.0	47.0	10.0	26.0	13.0	4.0	4.0	2.5	—
Pinus sabiniana	Digger pine	—	46.0	11.0	27.0	12.0	3.0	1.0	—	0.2
Pinus strobes	Eastern white pine	68.0	45.0	8.0	27.0	15.0	4.0	6.0	3.2	0.2
Pinus sylvestris	Scotch or Scots pine	—	47.0	11.0	28.0	—	1.0	—	1.6	0.2
Pinus taeda	Loblolly pine	68.0	45.0	12.0	27.0	11.0	2.0	3.0	2.0	—
Pseudotsuga menziesii	Douglas fir	66.0	45.0	8.0	27.0	13.0	4.0	4.0	1.3	0.2
Sequoia sempervirens	Redwood old growth	55.0	43.0	7.0	33.0	19.0	9.0	10.0	0.8	0.1
	Redwood second growth	61.0	46.0	7.0	33.0	14.0	5.0	<1.0	0.1	0.1
Taxodium distichum	Bald cypress	—	41.0	12.0	33.0	13.0	4.0	5.0	1.5	—
Thuja occidentalis	Northern white cedar	59.0	44.0	14.0	30.0	13.0	5.0	6.0	1.4	0.5
Thuja plicata	Western red cedar	—	38.0	9.0	32.0	21.0	11.0	14.0	2.5	0.3
Tsuga Canadensis	Eastern hemlock	—	41.0	9.0	33.0	13.0	4.0	3.0	0.5	0.5
Tsuga heterophylla	Western hemlock	67.0	42.0	9.0	29.0	14.0	4.0	4.0	0.5	0.4
Tsuga mertensiana	Mountain hemlock	60.0	43.0	7.0	27.0	12.0	5.0	5.0	0.9	0.5

Source: Pettersen, 1984.

TABLE 3.12
Polysaccharide Content of Some North American Woods

Scientific Name	Common Name	Glu	Xyl	Gal	Arab	Mann	Uronic	Acetyl	Lignin	Ash
Hardwoods										
Acer rubrum	Red maple	46	19	0.6	0.5	2.4	3.5	3.8	24	0.2
Acer saccharum	Sugar maple	52	15	<0.1	0.8	2.3	4.4	2.9	23	0.3
Betula alleghaniensis	Yellow birch	47	20	0.9	0.6	3.6	4.2	3.3	21	0.3
Betlula papyrifera	White birch	43	26	0.6	0.5	1.8	4.6	4.4	19	0.2
Fagus grandifolia	Beech	46	19	1.2	0.5	2.1	4.8	3.9	22	0.4
Liquidambar styraciflua	Sweetgum	39	18	0.8	0.3	3.1	—	—	24	0.2
Platanus occidentalis	Sycamore	43	15	2.2	0.6	2.0	5.1	5.5	23	0.7
Populus deltoides	Eastern cottonwood	47	15	1.4	0.6	2.9	4.8	3.1	24	0.8
Populus tremuloides	Quaking aspen	49	17	2.0	0.5	2.1	4.3	3.7	21	0.4
Quercus falcata	Southern red oak	41	19	1.2	0.4	2.0	4.5	3.3	24	0.8
Ulmus americana	White elm	52	12	0.9	0.6	2.4	3.6	3.9	24	0.3
Softwoods										
Abies balsamea	Balsam fir	46	6.4	1.0	0.5	12	3.4	1.5	29	0.2
Ginkgo biloba	Ginkgo	40	4.9	3.5	1.6	10	4.6	1.3	33	1.1
Juniperus communis	Juniper	41	6.9	3.0	1.0	9.1	5.4	2.2	31	0.3
Larix decidua	Larch	46	6.3	2.0	2.5	11	4.8	1.4	26	0.2
Larix laricina	Tamarack	46	4.3	2.3	1.0	13	2.9	1.5	29	0.2
Picea abies	Norway spruce	43	7.4	2.3	1.4	9.5	5.3	1.2	29	0.5
Picea glauca	White spruce	45	9.1	1.2	1.5	11	3.6	1.3	27	0.3
Picea mariana	Black spruce	44	6.0	2.0	1.5	9.4	5.1	1.3	30	0.3
Picea rubens	Red spruce	44	6.2	2.2	1.4	12	4.7	1.4	28	0.3
Pinus banksiana	Jack pine	46	7.1	1.4	1.4	10	3.9	1.2	29	0.2
Pinus radiata	Radiata pine	42	6.5	2.8	2.7	12	2.5	1.9	27	0.2
Pinus resinosa	Red pine	42	9.3	1.8	2.4	7.4	6.0	1.2	29	0.4
Pinus rigida	Pitch pine	47	6.6	1.4	1.3	9.8	4.0	1.2	28	0.4
Pinus strobus	Eastern white pine	45	6.0	1.4	2.0	11	4.0	1.2	29	0.2
Pinus sylvestris	Scots pine	44	7.6	3.1	1.6	10	5.6	1.3	27	0.4
Pinus taeda	Loblolly pine	45	6.8	2.3	1.7	11	3.8	1.1	28	0.3
Pseudotsuga menziesti	Douglas fir	44	2.8	4.7	2.7	11	2.8	0.8	32	0.4

(*Continued*)

TABLE 3.12
Polysaccharide Content of Some North American Woods (*Continued*)

Thuja occidentalis	Northern white cedar	43	10.0	1.4	1.2	8.0	4.2	1.1	31	0.2
Tsuga canadensis	Eastern hemlock	44	5.3	1.2	0.6	11	3.3	1.7	33	0.2

Source: Pettersen, 1984.

3.8.2.3 Apparatus

Buchner funnel
Extraction thimbles
Extraction apparatus, extraction flask (500 ml), Soxhlet extraction tube
Heating device, heating mantle or equivalent
Boiling chips, glass beads, boilers, or any inert granules for taming boiling action
Chemical fume hood
Vacuum oven

3.8.2.4 Reagents and Materials

Ethanol (ethyl alcohol), 200 proof
Toluene, reagent grade
Toluene-ethanol mixture, 1:1 (v/v)

3.8.2.5 Procedures

Weigh 2 to 3 grams of each sample into covered preweighed extraction thimbles. Place the thimbles in a vacuum oven not exceeding 45°C for 24 hours, or to constant weight. Cool the thimbles in a desiccator for one hour and weigh. Then place the thimbles in Soxhlet extraction units. Place 200 ml of the toluene:ethanol mixture in a 500-ml round-bottom flask with several boiling chips to prevent bumping. Carry out the extraction in a well-ventilated chemical fume hood for 2 hours, keeping the liquid boiling so that siphoning from the extractor is no less than four times per hour. After extraction with the toluene:ethanol mixture, take the thimbles from the extractors, drain the excess solvent, and wash the samples with ethanol. Place them in the vacuum oven over night at temperatures not exceeding 45°C for 24 hours. When dry, remove them to a desiccator for an hour and weigh. Generally, the extraction is complete at this stage; however, the extractability depends upon the matrix of the sample and the nature of extractives. Second and the third extractions with different polarity of solvents may be necessary. Browning (1967) suggests 4 hours of successive extraction with 95% alcohol, however, two successive extractions, four hours with ethanol followed with distilled water for 1 hour can also be done. Pettersen (1984) extracted pine sample with acetone/water, followed by the toluene/ethanol mixture.

3.8.3 Ash Content (ASTM D-1102-84)

3.8.3.1 Scope

The ash content of fiber is defined as the residue remaining after ignition at 575 ± 25°C for 3 hr, or longer if necessary to burn off all the carbon. It is a measure of mineral salts in the fiber, but it is not necessarily quantitatively equal to them.

3.8.3.2 Sample Preparation

Obtain a representative sample of the fiber, preferably ground to pass a 40-mesh screen. Weigh, to 5 mg or less, a specimen of about 5 g of moisture-free wood for ashing, preferably in duplicate. If the moisture in the sample is not known, determine it by drying a corresponding specimen to constant weight in a vacuum oven at 105 ± 3°C.

3.8.3.3 Apparatus

Crucible. A platinum crucible or dish with lid or cover is recommended. If platinum is not available, silica may be used.
Analytical balance having a sensitivity of 0.1 mg.
Electric muffle furnace adjusted to maintain a temperature of 575 ± 25°C.

3.8.3.4 Procedure

Carefully clean the empty crucible and cover, and ignite them to constant weight in a muffle furnace at 575 ± 25°C. After ignition, cool slightly and place in a desiccator. When cooled to room temperature, weigh the crucible and cover on the analytical balance.

Place all, or as much as practicable, of the weighed specimen in the crucible. Burn the sample directly over a low flame of a Bunsen burner (or preferably on the hearth of the furnace) until it is well carbonized, taking care not to blow portions of the ash from the crucible. If a sample tends to flare up or lose ash during charring, the crucible should be covered, or at least partially covered during this step. If the crucible is too small to hold the entire specimen, gently burn the portion added and add more as the flame subsides. Continue heating with the burner only as long as the residue burns with a flame. Place the crucible in the furnace at 575 ± 25°C for a period of at least 3 hr, or longer if needed, to burn off all the carbon. When ignition is complete, as indicated by the absence of black particles, remove the crucible from the furnace, replace the cover and allow the crucible to cool somewhat. Then place in a desiccator and cool to room temperature. Reweigh the ash and calculate the percentage based on the moisture-free weight of the fiber.

3.8.3.5 Report

Report the ash as a percentage of the moisture-free wood to two significant figures, or to only one significant figure if the ash is less than 0.1%.

3.8.3.6 Precision

The results of duplicate determinations should be suspect if they differ by more than 0.5 mg. Since the ignition temperature affects the weight of the ash, only values obtained at 575 ± 25°C should be reported as being in accordance with this method. Porcelain crucibles can also be used in most cases for the determination of ash. Special precautions are required in the use of platinum crucibles. There can be significant losses in sodium, calcium, irons and copper at temperatures over 600°C.

3.8.4 Preparation of Holocellulose (Chlorite Holocellulose)

3.8.4.1 Scope

Holocellulose is defined as a water-insoluble carbohydrate fraction of wood materials. According to Browning (1967) there are three ways of preparing holocellulose and their modified methods (1) Chlorination method, (2) Modified chlorination method, (3) Chlorine dioxide and chlorite method. The standard purity of holocellulose is checked following lignin analysis.

3.8.4.2 Sample Preparation

The sample should be extractive and moisture free and prepared after Procedure 9.2. If Procedure 9.2 is skipped for some reason, the weight of the extractives should be accounted for in the calculation of holocellulose.

3.8.4.3 Apparatus

Buchner funnel
250 ml Erlenmeyer flasks
25 ml Erlenmeyer flasks
Water bath
Filter paper
Chemical fume hood

3.8.4.4 Reagents

Acetic acid, reagent grade
Sodium chlorite, $NaClO_2$, technical grade, 80%

3.8.4.5 Procedure

To 2.5 g of sample, add 80 ml of hot distilled water, 0.5 ml acetic acid, and 1 g of sodium chlorite in a 250-ml Erlenmeyer flask. An optional 25-ml Erlenmeyer flask is inverted in the neck of the reaction flask. The mixture is heated in a water bath at 70°C. After 60 minutes, 0.5 ml of acetic acid and 1 g of sodium chlorite are added. After each succeeding hour, fresh portions of 0.5 ml acetic acid and 1 g sodium chlorite are added with shaking. The delignification process degrades some of the polysaccharides and the application of excess chloriting should be avoided. Continued reaction will remove more lignin but hemicellulose will also be lost (Rowell 1980).

Addition of 0.5 ml acetic acid, and 1 g of sodium chlorite is repeated until the wood sample is completely separated from lignin. It usually takes 6 to 8 hours of chloriting and the sample can be left without further addition of acetic acid and sodium chlorite in the water bath for over night. At the end of 24 hours of reaction, cool the sample and filter the holocellulose on filter paper using a Buchner funnel until the yellow color (the color of holocellulose is white) and the odor of chlorine dioxide is removed. If the weight of the holocellulose is desired, filter the holocellulose on a tarred fritted dics glass thimble, wash with acetone, vacuum oven dry at 105°C for 24 hours, place in a desiccator for an hour and weigh. The holocellulose should not contain any lignin and the lignin content of holocellulose should be determined and subtracted from the weight of the prepared holocellulose.

3.8.5 Preparation of Alpha-Cellulose (Determination of Hemicelluloses)

3.8.5.1 Scope

The preparation of α-cellulose is a continuous procedure from procedure 9.4. The term hemicellulose is defined as the cell wall components that are readily hydrolyzed by hot dilute mineral acids, hot dilute alkalies, or cold 5% sodium hydroxide.

3.8.5.2 Principle of Method

Extractive-free, lignin-free holocellulose is treated with sodium hydroxide and then with acetic acid, with the residue defined as α-cellulose. The soluble fraction represents the hemicellulose content.

3.8.5.3 Apparatus

A thermostat or other constant-temperature device will be required that will maintain a temperature of 20 ± 0.1°C in a container large enough to hold a row of at least three 250-ml beakers kept in an upright position at all times.

Filtering crucibles of Alundum or fritted glass thimbles of medium porosity.

3.8.5.4 Reagents

Sodium hydroxide (NaOH) solution, 17.5% and 8.3%
Acetic acid, 10% solution.

3.8.5.5 Procedure

Weigh out about 2 g of vacuum-oven dried holocellulose and place into a 250-ml glass beaker provided with a glass cover. Add 10 ml of 17.5% NaOH solution to the holocellulose in a 250-ml beaker, cover with a watch glass, and maintain at 20°C in a water bath. Manipulate the holocellulose lightly with a glass rod with a flat end so that all of the specimen becomes soaked with the NaOH solution. After the addition of the first portion of 17.5% NaOH solution to the specimen, at five minute intervals, add 5 ml more of the NaOH solution and thoroughly stir the mixture with the glass rod. Continue this procedure until the NaOH is consumed. Allow the mixture to stand at 20°C for 30 min. making the total time for NaOH treatment 45 min.

Add 33 ml of distilled water at 20°C to the mixture. Thoroughly mix the contents of the beaker and allow to stand at 20°C for 1 hour before filtering.

Filter the cellulose with the aid of suction into the tarred, alkali-resistant Alundum or fritted-glass crucible of medium porosity. Transfer all of the holocellulose residue to the crucible, and wash with 100 ml of 8.3% NaOH solution at 20°C. After the NaOH wash solution has passed through the residue in the crucible, continue the washing at 20°C with distilled water, making certain that all particles have been transferred from the 250-ml beaker to the crucible. Washing the sample in the crucible is facilitated by releasing the suction, filling the crucible to within 6 mm of the top with water, carefully breaking up the cellulose mat with a glass rod so as to separate any lumps present, and again applying suction. Repeat this step twice.

Pour 15 ml of 10% acetic acid at room temperature into the crucible, drawing the acid into the cellulose by suction but, while the cellulose is still covered with acid, release the suction. Subject the cellulose to the acid treatment for 3 min. from the time the suction is released; then apply suction to draw off the acetic acid. Without releasing the suction, fill the crucible almost to the top with distilled water at 20°C and allow to drain completely. Repeat the washing until the cellulose residue is free of acid as indicated by litmus paper. Give the cellulose a final washing by drawing, by suction, an additional 250 ml of distilled water through the cellulose in the crucible. Dry the crucible on the bottom and sides with a cloth and place it overnight in an oven to dry at 105°C. Cool the crucible and weighing bottle in a desiccator for 1 hr before weighing.

3.8.5.6 Calculation and Report

Calculate the percentage of α-cellulose on the basis of the oven-dried holocellulose sample, as follows:

$$\alpha\text{-cellulose, percent} = (W_2/W_1) \times 100$$

where

W_2 = weight of the oven-dried α-cellulose residue
W_1 = weight of the original oven-dried holocellulose sample

3.8.6 Preparation of Klason Lignin

3.8.6.1 Scope

Klason lignin gives a quantitative measure of the acid insoluble lignin and is not suitable for the study of lignin structures and some other lignins such as cellulolytic enzyme lignin, or Björkman (milled wood lignin) should be prepared (Sjöström 1981) for the study of lignin structure. This procedure is a modified version of ASTM D-1166-84. The lignin isolated using this procedure is also called sulfuric acid lignin.

3.8.6.2 Apparatus

Autoclave
Buchner funnel
100 ml centrifuge tube, Pyrex 8240
Desiccator
Glass rods
Water bath
Glass fiber
Filter paper, Whatman Cat No. 1827-021, 934-AH
Glass microfilter, 2.1 cm

3.8.6.3 Reagent

Sulfuric acid (H_2SO_4), 72% and 4% by volume
Fucose, 24.125% in 4% H_2SO_4 (w/w)

3.8.6.4 Procedure

Prepare samples by Procedure 9.2 and dry the sample at 45°C in a vacuum oven overnight. Accurately weigh out approximately 200 mg of ground vacuum-dried sample into a 100 ml centrifuge tube. To the sample in the 100 ml centrifuge tube, add 1 ml of 72% (w/w) H_2SO_4 for each 100 mg of sample. Stir and disperse the mixture thoroughly with a glass rod twice, then incubate the tubes in a water bath at 30°C for 60 min. Add 56 ml of distilled water. This results in a 4% solution for the secondary hydrolysis. Add 1 ml fucose internal standard (this procedure is required only if five sugars are to be analyzed by HPLC as a part of the analysis). Autoclave at 121°C and 15 psi, for 60 min. Remove the samples from the autoclave and filter off the lignin, with glass fiber filters (filters were rinsed into crucibles, dried and tarred) in crucibles using suction, keeping the solution hot. Wash the residue thoroughly with hot water and dry at 105°C overnight. Move to a desiccator, and let it sit an hour and weigh. Calculate Klason lignin content from weights.

3.8.6.5 Additional Information

Condensation reactions involving protein can cause artificially high Klason lignin measurements when tissues containing significant protein contents are analyzed. A nitrogen determination can be done to indicate possible protein content.

3.8.7 Determination of Methoxyl Groups

3.8.7.1 Scope

Methoxyl groups (–OCH3) are present in the lignin and lignin derivatives as side chains of aromatic phenylpropanes and in the polysaccharides mainly as methoxy uronic acids. Methoxyl content is determined using ASTM, D-1166-84.

3.8.7.2 Principle of Method

In the original method, methyl iodide was absorbed in an alcoholic solution of silver nitrate. The solution was diluted with water, acidified with nitric acid, and boiled. The silver iodide was removed by filtration, washed, and weighed in the manner usual for halide determinations. A volumetric modification is based on absorption of the methyl iodide in a known volume of standard silver nitrate solution and titration of the unused silver nitrate with standard potassium thiocyanate solution (ferric alum indicator solution). In this procedure, the methyl iodide is collected in an acetic acid solution of potassium acetate containing bromine.

$$CH_3I + Br_2 \rightarrow CH_3Br + IBr$$

$$IBr + 2Br_2 + 3H_20 \rightarrow HIO_3 + 5HBr$$

The excess bromine is destroyed by addition of acid, and the iodate equivalent of the original methoxyl content is determined by titration with sodium thiosulfate of the iodine liberated in the reaction:

$$HIO_3 + 5HI \rightarrow 3I_2 + 3H_2O$$

One methoxyl group is equivalent to six atoms of iodine and, consequently, a favorable analytical factor is obtained.

3.8.7.3 Sample Preparation

The sample is dried, ground, and extracted accordingly prior to analysis.

3.8.7.4 Apparatus

Reaction flask
Heat source
Vertical air-cooled condenser
Scrubber
Absorption vessels

3.8.7.5 Reagents

Bromine, liquid
Cadmium sulfate solution: Dissolve 67.2 g of $CdSO_4 \cdot 4H_2O$ in 1liter of water.
Carbon dioxide gas
Formic acid, 90%
Hydroiodic acid
Phenol
Potassium acetate solution in acetic acid. Anhydrous potassium acetate (100 g) is dissolved in 1 l of glacial acetic acid.
Potassium iodide solution-Dissolve 100 g of KI in water and dilute to 1 l.
Sodium acetate solution-Dissolve 415 g of sodium acetate trihydrate in water and dilute to 1 l.
Sodium thiosulfate solution (0.1 N)-Dissolve 25 g of $Na_2S_2O_3 \cdot H_2O$ in 200 ml of water and dilute to 1 l.
Starch indicator solution (10 g/l)
Sulfuric acid: Mix one volume of H_2SO_4 (sp gr 1.84) with nine volumes of water.

3.8.7.6 Procedure

Weigh the sample, about 100 mg of wood or 50 mg of lignin and place in the reaction flask. Place in the reaction flask 15 ml of HI, 7 g of phenol, and a boiling tube. Place in the scrubber a mixture of equal volumes of $CdSO_4$ solution and $Na_2S_2O_3$. The volume of solution should be adjusted so that the inlet tube of the scrubber is covered to a depth of about 4 mm. Adjust the flow of CO_2 to about 60 bubbles per minute through the scrubber. Heat the flask and adjust the rate of heating so that the vapors of the boiling HI rise about 100 mm into the condenser. Heat the flask under these conditions for 30 to 45 minutes, or longer if necessary, to remove methoxyl-containing or other interfering substances which are usually present in the reagents.

Let the distilling flask cool below 100°C. In the meantime, add to 20 ml of the potassium acetate solution, about 0.6 ml of bromine, and mix. Add approximately 15 ml of the mixture to the first receiver and 5 ml to the second, and attach the receiver to the apparatus. Seal the ground-glass joint with a small drop of water from a glass rod.

Remove the distilling flask and introduce the test specimen. Immediately reconnect the flask and seal the ground-glass joint with a drop of molten phenol from a glass rod. Bring the contents of the flask to reaction temperature while passing a uniform stream of CO_2 through the apparatus.

Adjust the rate of heating so that the vapors of the boiling HI rise about 100 ml into the condenser. Continue the heating for a time sufficient to complete the reaction and sweep out the apparatus. Usually, not more than 50 minutes are required.

Wash the contents of both receivers into a 250-ml Erlenmeyer flask that contains 15 ml of sodium acetate solution. Dilute with water to approximately 125 ml and add 6 drops of formic acid. Rotate the flask until the color of the bromine is discharged, then add 12 more drops of formic acid and allow the solution to stand for 1 to 2 min. Add 10 ml of KI solution and 10 ml of H_2SO_4, and titrate the liberated iodine with $Na_2S_2O_3$ solution, adding 1 ml of starch indicator solution just before the end point is reached, continuing the titration to the disappearance of the blue color.

3.8.7.7 Calculation and Report

$$\text{Methoxyl, \%} = (VN \times 31.030 \times 100)/(G \times 1000 \times 6) = (VN/G) \times 0.517$$

where:

V = milliliters of $Na_2S_2O_3$ solution required for the titration,
N = normality of $Na_2S_2O_3$ solution, and
G = grams of moisture free sample.

Table 3.9 shows the methoxyl content of some common hardwoods and softwoods.

3.8.8 Determination of Acetyl by Gas Liquid Chromatography

3.8.8.1 Scope

The acetyl and formyl groups that are in the polysaccharide portion can be determined in one of three ways: (1) acid hydrolysis; sample is hydrolyzed to form acetic acid, (2) saponification; acetyl groups are split from polysaccharides with hot alkaline solution and acidified to form acetic acid, or (3) trans-esterificaion; sample is treated with methanol in acid or alkaline solution to form methyl acetate. Acetic acid and methyl acetate are analyzed by gas chromatography.

The procedure presented here is saponification and acetyl determined by gas chromatography.

$$CH_3COOR + NaOH \rightarrow CH_3COONa + ROH$$

$$CH_3COONa + H+ \rightarrow CH_3COOH$$

3.8.8.2 Reagents

Formic acid, 2%: Dilute 2 ml of 90% formic acid to 900 ml with deionized H_2O.
Internal standard stock solution: Weigh 25.18 grams of 99+% proprionic acid in 500 ml volumetric flask, make to volume with 2% formic acid.
Internal standard solution: Pipette 10 ml stock solution into a 200-ml volumetric flask, make to volume with deionized water.
Acetic acid standard solution: Weigh 100 mg 99.7% glacial acetic acid into a 100-ml volumetric flask, make to volume with deionized water.
NaOH solution l N: Weigh 4 grams sodium hydroxide, dissolve in 100 ml deionized water.

3.8.8.3 Sample Preparation

The amount of sample is based on the approximate acetyl content: Acetyl content (AC) 0–10%, 50 mg; AC 10%, 25 mg; AC 15%, 20 mg; AC 20%, 15 mg; AC 25%, 10 mg. Weigh an oven-dried sample in a long-handled weighing tube and transfer it to an acetyl digestion flask and add boiling chips. Pipette 2 ml l N NaOH solution to wash down the neck of the flask. Connect the reaction flask to a water cooled reflux condenser and reflux for 1 hour. Cool the reaction flask to room temperature and pipette 1 ml of propionic acid (internal standard) into a 10 ml volumetric flask. Quantitatively transfer the liquid from the reaction flask to the volumetric flask. Wash the reaction flask and the solid residue with several portions of distilled water. Add 0.2 ml of 85% phosphoric acid and make to volume with distilled water. This solution may be filtered through a small plug of glass wool to remove solid particles. Analyze the sample by GLC and determine the average ratio. Milligrams of acetic acid are determined from the calibration curve.

3.8.8.4 Gas Chromatography

Column: Supelco 60/80 Carbopack C/0.3% carbowax 20 M/0.1% H_3P0_4 - 3 ft 1/4 inch O. D. and 4 mm I. D.; Oven temperature 120°C; Injection port 150°C; F.I.D. 175°C; Nitrogen 20 ml/min.

The ratio of the area is determined by dividing the area of the acetic acid by the area of the propionic acid (internal standard). The average of the ratios is used to determine mg/ml of acetic acid from the calibration curve.

Preparation of a calibration curve: Pipette 1, 2, 4, 6, and 8 ml of standard acetic acid solution into 10 ml volumetric flasks. Pipette 1 ml of propionic acid internal standard into each sample, then add 0.2 ml 85% phosphoric acid. Make to volume with distilled water. Analyze each solution three times by GLC. Calculate the ratios by dividing the area of the acetic acid by the area of the propionic acid (internal standard). Plot the average ratios against milligrams per milliliter of acetic acid. Standard and sample solutions can be stored in the refrigerator for at least 1 week.

3.8.8.5 Reporting

Report the average, standard deviation and precision of each sample. The results may be reported as percent acetic acid or as percent acetyl:

$$\% \text{ acetic acid} = \frac{\text{mg/ml acetic acid found} \times 10 \text{ ml} \times 100}{\text{sample weight in mg}}$$

$$\% \text{ acetyl} = \% \text{ acetic acid} \times 0.7172$$

TABLE 3.13
Chemical Composition of Selected Hardwoods from the Southeastern United States (Percent of Oven-Dry Wood)

		Carbohydrates		Components of Hemicelluloses						
Scientific Name	Common Name	Cell	Total Hemi	Gluco Mann	AcGlu UrXyl	Arab Gal	Pectin	Lignin	Total Ext	Ash
Acer rubrum	Red maple	40.7	30.4	3.5	23.5	1.6	1.9	23.3	5.3	0.3
Aesculus octandra	Yellow buckeye	40.6	25.8	3.6	18.6	1.0	2.6	30.0	3.1	0.5
Carya glabra	Pignut hickory	46.2	26.7	1.1	22.1	1.2	2.3	23.2	3.4	0.6
Carya illinoensis	Pecan	38.7	30.2	1.6	24.7	1.6	2.3	23.2	3.4	0.6
Carya tomentosa	Mockernut	43.5	27.7	1.5	21.5	1.3	3.5	23.6	5.0	0.4
Cornus florida	Flowering dogwood	36.8	35.4	3.4	27.2	1.0	5.0	21.8	4.6	0.3
Fagus grandifolia	American beech	36.0	29.4	2.7	23.5	1.3	1.8	30.9	3.4	0.4
Fraxinus americana	White ash	39.5	29.1	3.8	22.1	1.4	1.9	24.8	6.3	0.3
Gordonia lasianthus	Loblolly-bay	43.8	29.1	4.1	22.1	1.1	1.8	21.5	5.2	—
Liquidambar styraciflua	Sweetgum	40.8	30.7	3.2	21.4	1.3	4.9	22.4	5.9	0.2
Liriodendron tulipifera	Yellow poplar	39.1	28.0	4.9	20.1	0.7	2.4	30.3	2.4	0.3
Magnolia virginiana	Sweetbay	44.2	37.7	4.3	20.2	1.6	1.6	24.1	3.9	0.2
Nyssa aquatica	Water tupelo	45.9	24.0	3.5	18.6	0.8	1.1	25.1	4.7	0.4
Nyssa sylvatica	Black tupelo	42.6	27.3	3.6	18.0	1.0	4.8	26.6	2.9	0.6
Oxydendron arboreum	Sourwood	40.7	34.6	1.3	31.9	1.0	0.4	20.8	3.6	0.3
Persea borbonia	Redbay	45.6	25.6	1.0	23.2	0.9	0.5	23.6	5.0	0.2
Platunus occidentalis	Sycamore	43.0	27.2	2.3	22.3	1.4	1.2	25.3	4.4	0.1
Populus deltoids	Eastern cottonwood	46.5	26.6	4.4	16.8	1.6	1.8	25.9	2.4	0.6
Quercus alba	White oak	41.7	28.4	3.1	21.0	1.6	2.7	24.6	5.3	0.2
Quercus coccinea	Scarlet oak	43.2	29.2	2.3	23.3	1.4	2.2	20.9	6.6	0.1
Quercus falcata	Southern red oak	40.5	24.2	1.7	18.6	1.7	2.2	23.6	9.6	0.5

(Continued)

TABLE 3.13
Chemical Composition of Selected Hardwoods from the Southeastern United States (Percent of Oven-Dry Wood) (*Continued*)

Scientific Name	Common Name	Carbohydrates		Components of Hemicelluloses			Pectin	Lignin	Total Ext	Ash
		Cell	Total Hemi	Gluco Mann	AcGlu UrXyl	Arab Gal				
Quercus ilicifolia	Scrub oak	37.6	27.5	1.0	22.3	1.8	2.4	26.4	8.0	0.5
Quercus marylandica	Blackjack oak	33.8	28.2	2.0	21.0	2.3	2.9	30.1	6.6	1.3
Quercus nigra	Water oak	41.6	34.8	3.0	28.9	2.2	0.7	19.1	4.3	0.3
Quercus prinus	Chestnut oak	40.8	29.9	2.9	23.8	1.8	1.4	22.3	6.6	0.4
Quercus rubra	Northern red oak	42.2	33.1	3.3	26.6	1.6	1.6	20.2	4.4	0.2
Quercus stellata	Post oak	37.7	29.9	2.6	23.0	2.0	2.3	26.1	5.8	0.5
Quercus velutina	Black oak	39.6	28.4	1.9	23.2	1.1	1.9	25.3	6.3	0.5
Quercus virginiana	Live oak	38.1	22.9	1.0	18.3	1.7	1.9	25.3	13.2	0.6
Sassafras albidum	Sassafras	45.0	35.1	4.0	30.4	0.9	<0.1	17.4	2.4	0.2
Ulmus americana	American elm	42.6	26.9	4.6	19.9	0.8	1.6	27.8	1.9	0.8

Cell = Cellulose.

Source: Pettersen, 1984.

TABLE 3.14
Elemental Composition of Some Woods

Scientific Name	Common Name	Ca ppt	K ppt	Mg ppt	P ppt	Mn ppt	Fe ppm	Cu ppm	Zn ppm	Na ppm	Cl ppm
Abies balsamea	Balsam fir	0.8	0.8	0.27	—	0.13	13	17	11	18	—
Acer rubrum	Red maple	0.8	0.7	0.12	0.03	0.07	11	5	29	5	18
Betula papyrifera	White birch	0.7	0.3	0.18	0.15	0.03	10	4	28	9	10
Fraxinus americana	White ash	0.3	2.6	1.8	0.01	—	—	—	—	31	—
Liquidambar styraciflua	Sweetgum	0.55	0.3	0.34	0.15	0.08	—	—	19	81	—
Picea rubens	Red spruce	0.8	0.2	0.07	0.05	0.14	14	4	8	8	0.3
Pinus strobes	Eastern white pine	0.2	0.3	0.07	—	0.03	10	5	11	9	19
Populus deltoids	Eastern cottonwood	0.9	2.3	0.29	—	0.2	100	—	30	940	—
Populus tremuloides	Quaking aspen	1.1	1.2	0.27	0.10	0.03	12	7	17	5	—
Quercus alba	White oak	0.5	1.2	0.31	—	<0.01	—	—	—	21	15
Quercus falcate	Southern red oak	0.3	0.6	0.03	0.02	0.01	30	73	38	44	—
Tilia americana	Basswood	0.1	2.8	0.35	—	—	—	—	—	63	38
Tsuga canadensis	Eastern hemlock	1.0	0.4	0.11	0.12	0.15	6	5	2	6	—

Source: Pettersen, 1984.

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