
3 Cell Wall Chemistry

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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).

A complete chemical analysis accounts for all the components of wood. Vast amounts of data are available on the chemical composition of wood. All tables in this chapter 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

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

Species	Holocellulose	-cellulose	Hemicellulose	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: Adapted from Pettersen, R.C. 1984. *The Chemistry of Solid Wood*, Advances in Chemistry Series 20, Chapter 2, pp. 57–126, Washington, DC: ACS.

of cellulose (40–45%) and the hemicelluloses (15–25%) are called holocellulose and usually accounts for 65–70% 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. Actually the building block for cellulose is 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 minimized depolymerization and maximized yield. These molecular weight determinations, done by light-scattering experiments, indicate the wood cellulose has an average DP of at least 9000–10,000 and possibly as high as 15,000. An average DP of 10,000 would mean a linear chain length of approximately 5 μ m 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.

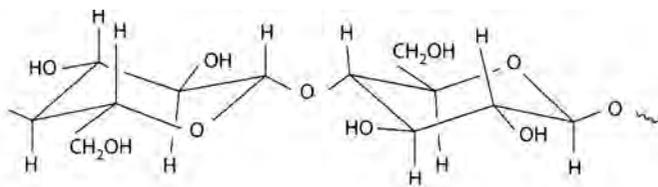


FIGURE 3.1 Chemical structure of cellobiose.

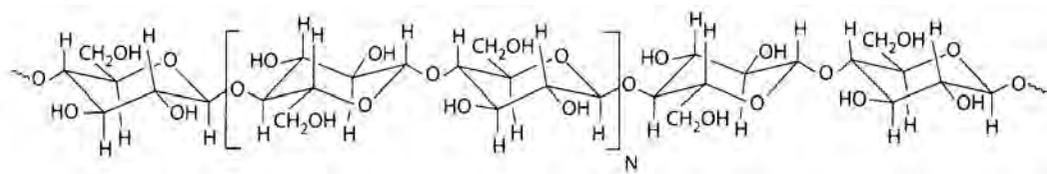


FIGURE 3.2 Partial structure of cellulose.

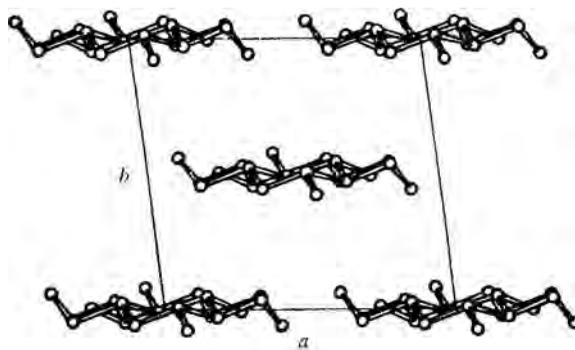


FIGURE 3.3 Axial projection of the crystal structure of cellulose I.

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 crystalline cellulose (*Valonia ventricosa*) has a space group symmetry $a = 16.34 \text{ \AA}$ and $b = 15.72 \text{ \AA}$ (Figure 3.3, Gardner and Blackwell 1974). The distance of one repeating unit, that is, one cellobiose unit is $c = 10.38 \text{ \AA}$ (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 above) and accessible and nonaccessible. Accessible and nonaccessible celluloses refer to the availability of the cellulose to water, microorganisms, and so on. The surfaces of crystalline cellulose are accessible

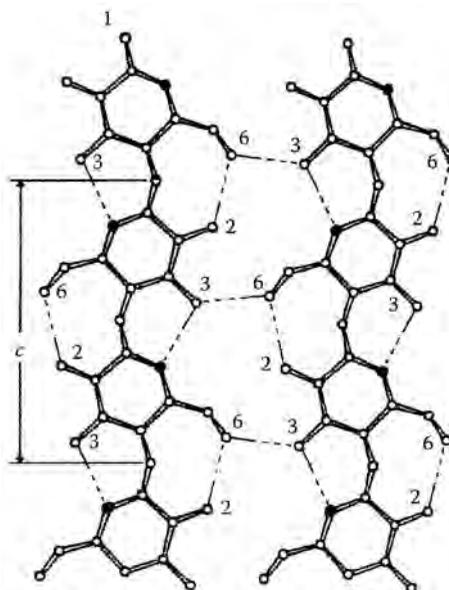


FIGURE 3.4 Planar projection of two cellulose chains showing some of the hydrogen bond between cellulose chains and within a single cellulose chain.

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 as cellulose II. Cellulose II is obtained by mercerization and regeneration of native cellulose. Mercerization is treatment of cellulose I with strong alkali. Regeneration is a 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 $a = 8.01 \text{ \AA}$, $b = 9.04 \text{ \AA}$ (Figure 3.3), and $c = 10.36 \text{ \AA}$ (Figure 3.4).

There is also cellulose III which is treatment of cellulose I with liquid ammonia at about -80°C 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 260°C .

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 cellulose referred to as Kurschner cellulose also based on the method of isolation. Kurschner cellulose is obtained by refluxing wood meal three times for 1 h with a 1:4 (v/v) mixture of nitric acid and ethyl alcohol. The water washed and dried cellulose is referred to as Kurschner 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 make the cellulose to swell 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.

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 designation D and L refer to a standard configuration for the two optical isomers of glyceraldehydes, the simplest carbohydrate, and designate the conformation of the hydroxyl group at carbon four for pentoses (xylose and arabinose) and carbon five for hexoses (glucose, galactose, and mannose). The Greek letters α and β refer to the configuration of the hydroxyl group on carbon one. The two configurations are called anomers. The first entry is a shortened form of the sugar name. The second entry 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 entry is an abbreviation commonly used for a sugar residue in a polysaccharide (Whistler et al. 1962, Timell 1964, 1965, Whistler and Richards 1970, Jones et al. 1979).

Hemicelluloses are intimately associated with cellulose and contribute to the structural component on the tree. Some hemicelluloses are present in very large amounts when the tree is under stress, that is, compression wood where the wood has a higher D-galactose content as well as a

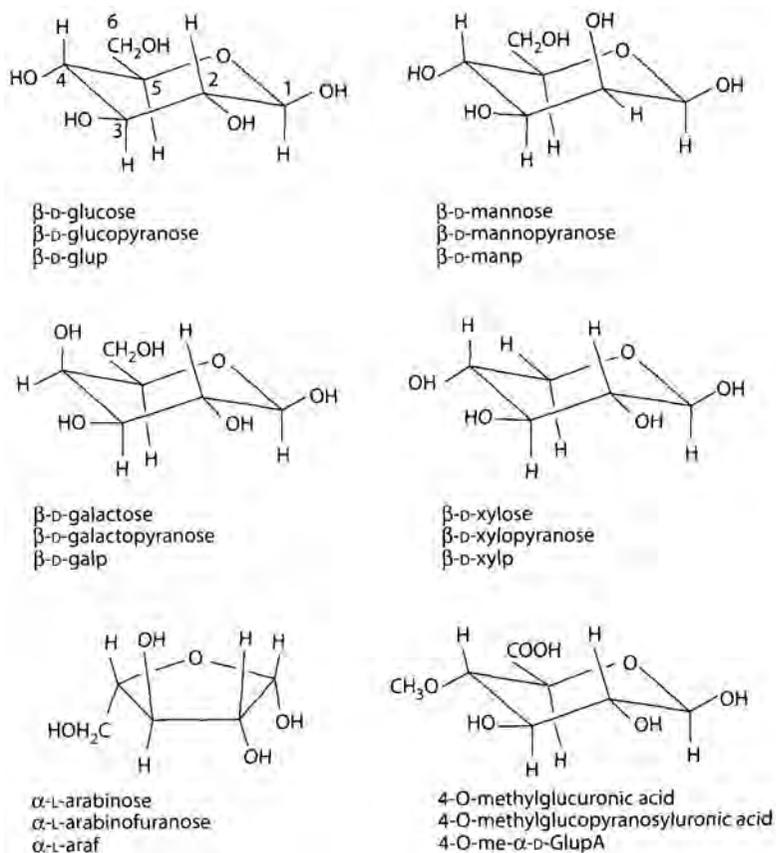


FIGURE 3.5 Sugar monomer components of wood hemicellulose.

higher lignin content (Timell 1982). They usually contain a backbone consisting of one repeating sugar unit linked β -(1 \rightarrow 4) with branch points (1 \rightarrow 2), (1 \rightarrow 3), and/or (1 \rightarrow 6).

Hemicelluloses usually consist of more than one type of sugar unit and are sometimes referred to by the sugars they contain, for example, galactoglucomannan, arabinoglucuronoxylan, arabinogalactan, glucuronoxylan, glucomannan, and so on. 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 wood. The hemicelluloses can then be precipitated from the alkaline solution by acidification using acetic acid. Further treatment with a neutral organic solvent such as ethyl alcohol to the neutralized solution results in a more complete precipitation (Sjöström 1981). The detailed structures of most wood hemicelluloses have not been determined. Only the ratio of sugars these polysaccharides contain have been studied.

3.1.3.1 Hardwood Hemicelluloses

Figure 3.6 shows a partial structure of 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 \rightarrow 4) with acetyl groups at C-2 or C-3 of the xylose units on an average of 7 acetyls per 10 xylose units (Sjöström 1981). The xylan is substituted with side chains of 4-O-methylglucuronic acid units linked to the xylan backbone α -(1 \rightarrow 2) with an average frequency of approximately 1 uronic acid group per 10 xylose units. The side chains are quite short.

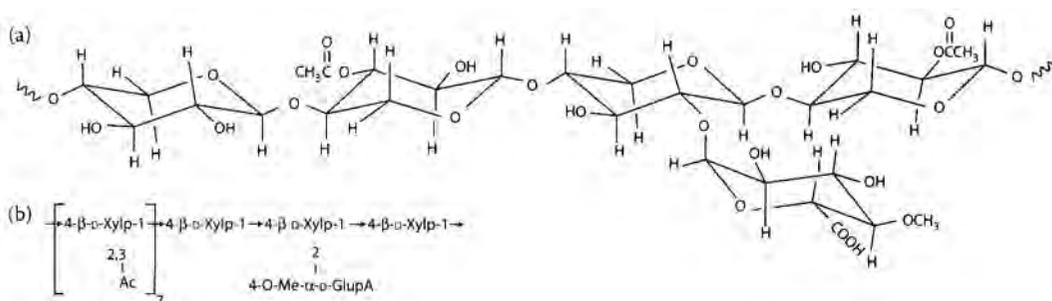


FIGURE 3.6 Partial molecular structure (a) and structure representation (b) of O-acetyl-4-O-methylglucuronoxylan.

TABLE 3.2

Major Hemicelluloses in Hardwoods

Hemicellulose Type	Percent in Wood	Units	Molar Ratio	linkage	DP
Glucuronoxylan	15–30	β -D-xylop	10	1 \rightarrow 4	200
		4-O-Me- α -D-GlupA	1	1 \rightarrow 2	
		Acetyl	7		
Glucomannan	2–5	β -D-Manp	1–2	1 \rightarrow 4	200
		β -D-Glup	1	1 \rightarrow 4	

Hardwoods also contain 2–5% of a glucomannan composed of β -D-glucopyranose and β -D-mannopyranose units linked (1 \rightarrow 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.

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 (ca. 20%) with a linear or possibly slightly branched chain with β -(1 \rightarrow 4) linkages (Figure 3.7). Glucose and mannose make up the backbone polymer with branches containing galactose. There are two fractions of these polymers differing by their galactose content. The low galactose fraction has a ratio of galactose:glucose:mannose of about 0.1:1:4 while the high galactose fraction has a ratio of 1:1:3. The D-galactopyranose units are linked as a single unit side chain by α -(1 \rightarrow 6) bonds. The 2- and 3-positions of the backbone polymer have acetyl groups substituted on them an average of 3–4 hexose units.

Another major hemicellulose polymer in softwoods (5–10%) is an arabinoglucuronoxylan consisting of a backbone of β -(1 \rightarrow 4) xylopyranose units with a (1 \rightarrow 2) branches of D-glucopyranosyluronic acid on the average of every 2–10 xylose units and α -(1 \rightarrow 3) branches of L-arabinofuranose on the average of 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 \rightarrow 3)-linked D-galactopyranose polymer with almost every unit having a branch attached to carbon 6 of β -D-galactopyranose residues. In some cases this side chain is β -L-arabinofuranose linked (1 \rightarrow 3) or β -D-arabinopyranose linked (1 \rightarrow 6).

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 \rightarrow 4) (amylose) or α -(1 \rightarrow 4) with branches about every 25 glucopyranosyl units at α -(1 \rightarrow 6) (amylopectin). Amylose occurs as a helix structure in the solid state due to the a-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 (Adler 1977).

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

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 type 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%, where 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–guaiacyl lignin” as they are a copolymer of coniferyl and sinapyl alcohols. The ratio of these two varies in different lignins from a ratio of 4:1 to 1:2 (Sarkanen and Ludwig 1971). A proposed structure for a hardwood lignin (*Fagus sylvatica* 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. The so-called Klason lignin is obtained after hydrolyzing the polysaccharides with 72% sulfuric acid. It is highly condensed and does not truly

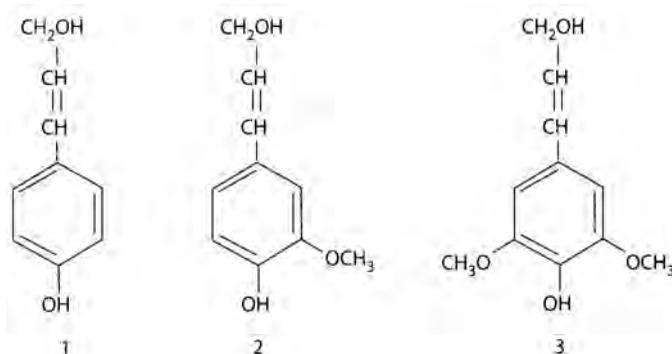


FIGURE 3.9 Chemical structures of lignin precursors, 1 = *p*-coumaryl alcohol, 2 = coniferyl alcohol, and 3 = sinapyl alcohol.

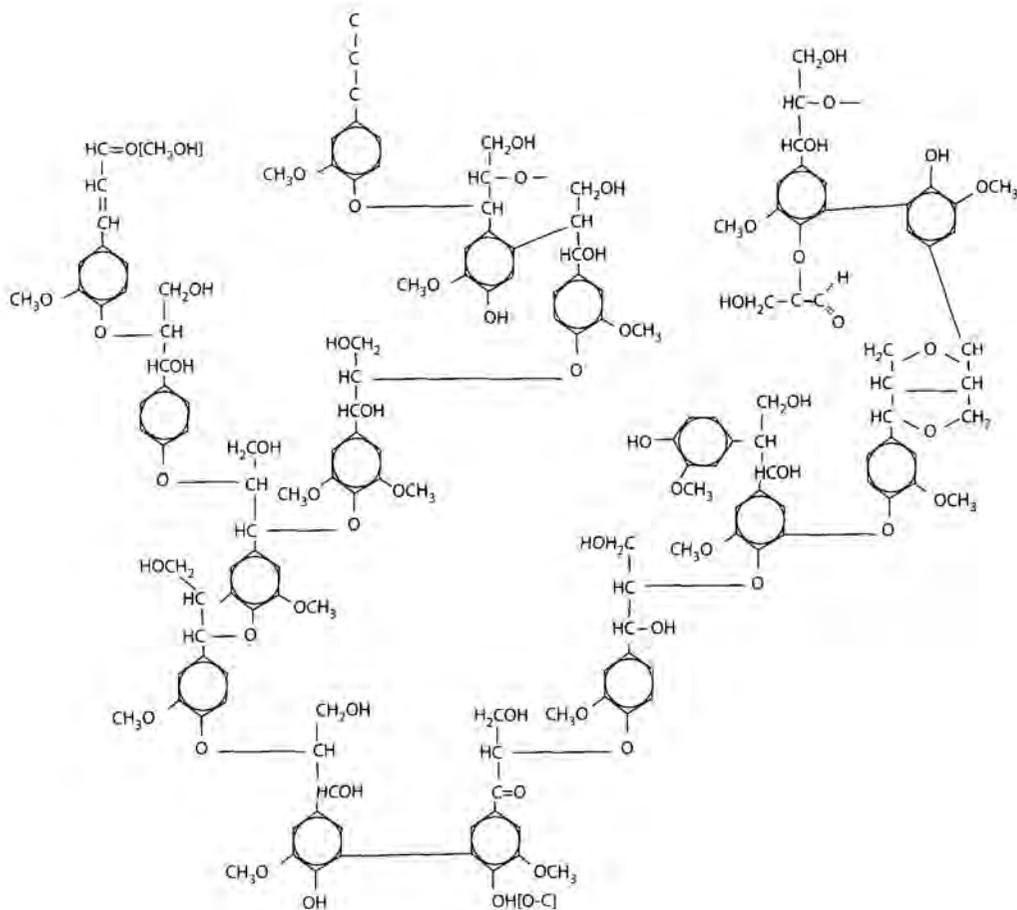


FIGURE 3.10 Partial structure of a softwood lignin.

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 extracted with suitable organic solvents (Björkman 1956, 1957). Approximately, 30–50% of the native lignin is isolated using this procedure. This is a tedious procedure 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 from 260 to 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 several solvents. In some cases, the extractives are classified by the solvent used to extract them, for example, water-soluble or toluene–ethanol 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

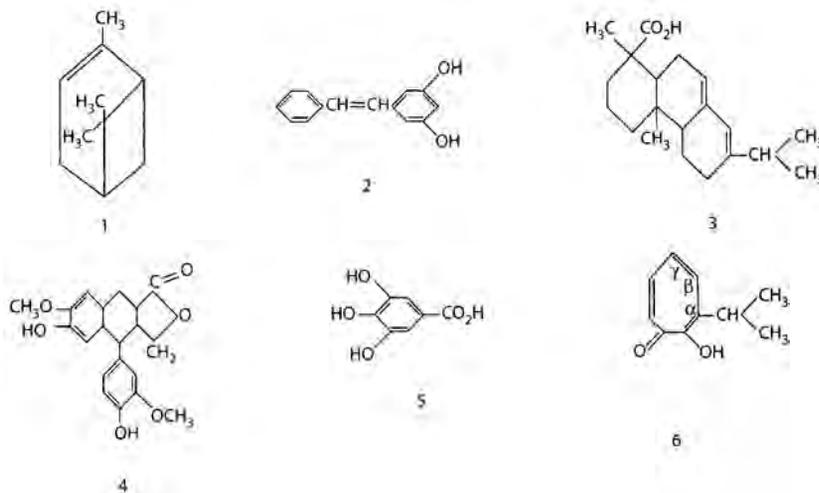


FIGURE 3.11 Chemical structures of some of the extractives in wood. 1 = abietic acid, 2 = α -pinene, 3 = pinosylvin, 4 = pinoresinol, 5 = gallic acid, and 6 = α -, β -, and γ -thujaplicin.

pitch and resins, have been used for centuries to waterproof wooden boats, used 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 in response to wounds, and some act as 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 higher extractives content than hardwoods and most of the extractives in both softwoods and hardwoods are located in the heartwood and some are responsible for the color, smell, and durability. 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 acid 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 function are mainly found in heartwood (Kai 1991). Abietic acid (Figure 3.11-1) is a common type of resin acid.

The most common terpene in softwoods is α -pinene (Figure 3.11-2) and other similar chemical structures. One of the most important polyphenols is pinosylvin (Figure 3.11-3) 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 3.11-4) is found in spruce and hemlock. Tannins in wood can be classified into three classes: gallotannins, ellagitannins, and condensed tannins (Hemingway 1989, Porter 1989). Gallotannins are polymeric esters of gallic acid (Figure 3.11-5) and are usually associated with sugars (Haslam 1989). Tropolones are responsible for the durability of cedar wood. α -, β -, and γ -Thujaplicin (Figure 3.11-6) are examples of this class of extractives (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 is also known as the periderm, and is made up of three layers: the phellem (cork cells), phellogen (cork cambium), and the phellogen (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

TABLE 3.4

Average Chemical Composition of Softwood and Hardwood Bark

Component	Percent Oven-Dry Weight	
	<i>Pinus pinaster</i> ^a	<i>Quercus suber</i> ^b
Polysaccharides	41.7±10.9	19.9±2.6
Lignin and polyphenols	43.7±12.4	23.0±0.5
Suberin	1.5±0.2	39.4±1.7
Extractives	11.4±12.2	14.2±1.1
Ash	1.2±0.6	1.2±0.2

^a Data obtained from Nunes, E., Quilhó, T., and Pereira, H. 1996. Anatomy and chemical composition of *Pinus pinaster* bark. *IAWA Journal* 17(2): 141-149.

^b Data obtained from Pereira, H. 1988. Chemical composition and variability of cork from *Quercus suber* L. *Wood Sci. Technol.* 22: 211-218.

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 equally complex, and varies between and within species, and also between the inner and outer bark (Toman et al. 1976). 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 (NaOH) 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 which interfere with these analysis methods. For example, 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.

Owing to 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 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 NaOH 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 polishes, lubricants, additives to concrete, carbon papers and fertilizers, and in fruit coatings (Hemingway 1981).

Terpenes are a condensation of two or more 5-carbon isoprene (2-methyl-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% of the 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).

Hydrolysable and condensed tannins are also major extractives from bark. The hydrolysable tannins are esters of carboxylic acids and sugars that are easily hydrolyzed to give benzoic acid derivatives and sugars. Over 20 different hydrolysable 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 DP tannins are soluble in polar solvents whereas the high DP 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 mainly composed of glucose and fructose and 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 are tied up 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 and arabino-4-O-methyl-glucuronoxylan 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-methyl-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 to 1 with a DP of between 171 and 234 (Mian and Timell 1960). Glucomannans from deciduous barks contain mannose and glucose units in a ratio of about 1:1 to 1.4:1 (Timell 1961b). The mannans from the barks of aspen and willow, galactose

TABLE 3.5
Sugars Present in Hydrolysates of Some Tree Barks

Species	Glu	Man	Gal	Xyl	Ara	Rha	UrA	Ac
<i>Abies amabilis</i>	37.4	8.0	1.6	3.2	3.2	—	5.6	0.8
<i>Picea abies</i>	36.6	6.5	1.3	4.8	1.8	0.3	—	—
<i>Picea engelmannii</i>	35.7	2.9	2.4	3.8	3.3	—	8.0	0.5
<i>Pinus contorta</i>								
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
<i>Pinus sylvestris</i>	30.2	5.4	2.4	5.8	2.1	0.3	—	—
<i>Pinus taeda</i>								
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	—
<i>Betula papyrifera</i>								
Inner bark	28.0	0.2	1.0	21.0	2.7	—	2.2	—
<i>Fugus sylvatica</i>	29.7	0.2	3.1	20.1	3.1	1.2	—	—
<i>Quercus robur</i>	32.3	0.5	1.3	16.4	2.0	0.5	—	—

Source: Adapted from Fengel, D. and Wegener, G. 1984. *Wood: Chemistry, Ultrastructure and Reactions*. W. de Gruyter, Berlin.

units were found as side chains. The ratio of manose:glucose:galactose was 1.3:1:0.5 with an average DP of 30–50 (Timell 1961b).

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 DP is 95 (Timell 1961b). A group of galacturonic acid polymers has been isolated from birch. One is a galacturonic acid backbone α -(1 \rightarrow 4) with arabinose side chains in a ratio of galacturonic acid to arabinose of 9:1 and another one consisting 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 1961b).

A pectic substance has been isolated from barks, which contains either galactose alone or galactose and arabinose units (Toman et al. 1976). The pure galactan is water-soluble and consists of 33 β -(1 \rightarrow 4)-linked galactose units with side chains at C6 of the backbone. A highly branched arabinogalactan was found in the bark of spruce bark 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 the composition.

Table 3.5 shows the sugars present after hydrolysis of the polysaccharides in bark.

3.4.3 CELLULOSE

The cellulose content of barks ranges from 16% to 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 extractive 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 DP 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 hydrolysable 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% to 58% (Labosky 1979). The elemental composition and functional group content of bark lignins are similar to 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 the 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 (Anderson et al. 1973). While there are some differences in the ratio 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, Harder and Einspahr 1980). For example, the outer bark of willow contains 11.5% ash, the inner bark 13.1% compared to 0.9% in sapwood; sweetgum outer 10.4%, inner 12.8%, sapwood 0.5%; red oak outer 8.9%, inner 11.1%, sapwood 0.9%; and, ash, outer 12.3%, inner 12.1%, sapwood 0.9%. 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 normal wood due to the higher inorganic content of bark compared to normal wood. For example, Martin and Gray (1971) reported the pH values of southern pines ranging from about 3.1 to 3.8 with an average of 3.4 to 3.5 compared to a pH of 4.4 to 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 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 $575 \pm 25^\circ\text{C}$. 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 existed as oxalates, carbonates, and sulfates in the wood 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 within and between species. The inorganic content varies depending on the environmental conditions in which the tree lives. See Tables 3.11 through 3.13 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 energy-dispersive x-ray analysis (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 early wood as compared to late wood.

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 IN 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 springwood. 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 and encrustation of pit membranes with the formation of tyloses occurs in hardwoods. Springwood contains more lignin than summerwood.

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 (0.7%). The S₁ layer is composed of 51.7% lignin, 30.0% cellulose, and 18.3% hemicelluloses. The S₂ layer is composed of 15.1% lignin, 54.3% cellulose, and 30.6% hemicelluloses. The S₃ layer has little or no lignin, 13% cellulose, and 87% hemicelluloses. The content of xylan is lowest in the S₂ layer and higher in the S₁ and S₃ layers. The concentration of galactoglucomannan is higher in the S₂ than the S₁ or S₃ layers. On a percentage basis, the middle lamella and primary wall contain the highest concentration of lignin but there is more lignin in the S₂ because it is a much thicker layer as compared to the middle lamella and primary wall. The lignin in the S₂ 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 S₂ layer is 14–19°. It is because this angle is so low in the thick S₂ layer that wood does not swell or shrink (0.1–0.3%) in the longitudinal direction.

Figure 3.13 shows more detail of the cell wall. It shows possible lignin–carbohydrate bonding and very little, if any, contact between lignin and cellulose.

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: Adapted from Saka, S. 1991. *Wood and Cellulosic Chemistry*, Chapter 2, pp. 59–88, New York, NY: Marcel Dekker, Inc.

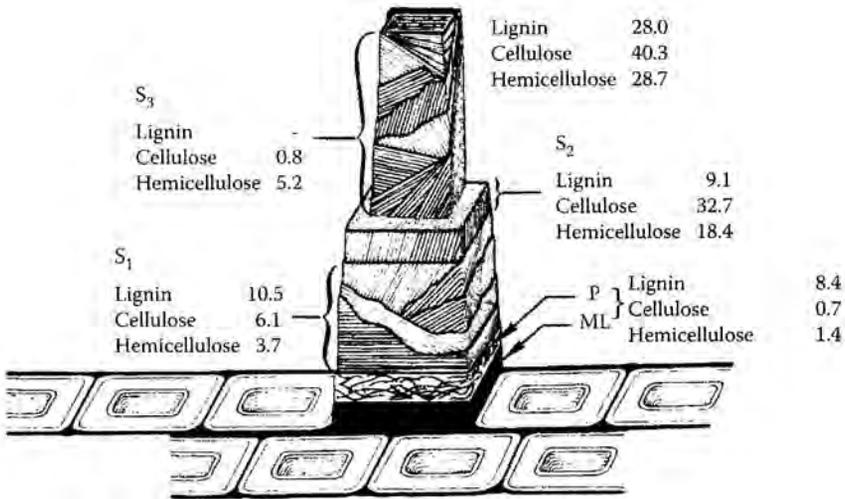


FIGURE 3.12 Chemical composition of the cell wall of scots pine.

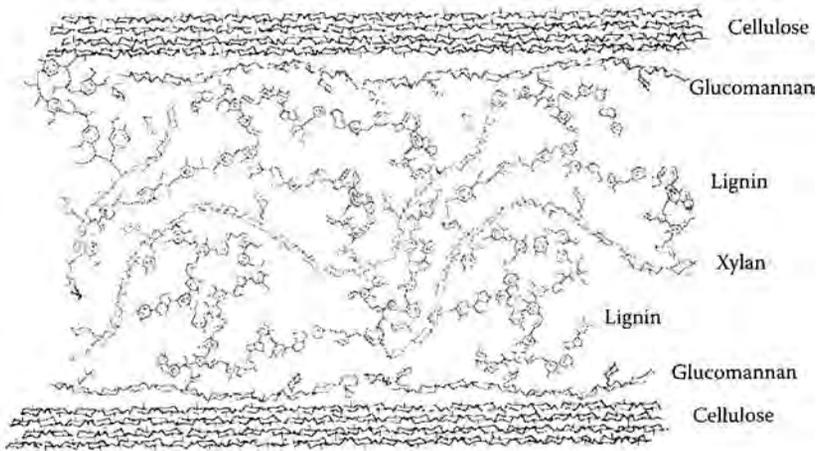


FIGURE 3.13 Schematic of the wood cell wall.

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 (Chapter 11).

3.7 JUVENILE WOOD AND REACTION WOOD

Juvenile wood is the wood that develops in the early stages of tree growth. Its physical properties are described in the chapter. Juvenile wood cells are shorter, have smaller cell diameter, larger microfibril angle (up to 55°) 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 matures.

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 higher lignin content and lower cellulose content as compared to normal wood. The cellulose in the S₂ layer has a lower degree of crystallization than normal wood and the lignin is largely concentrated in the S₂ layer as compared to normal wood. Forty percent of the lignin is in the outer zone of the S₂ layer and an additional 40% is uniformly distributed over the remaining part of the S₂ layer (Panshin and de Zeeuw 1980). There are more galactoglucomannans in normal wood and more 1 → 3 linked glucans and galactans in compression wood. The microfibril angle in the modified S₂ layer in compression wood is quite high (44–47°) and have more rounded tracheids that are 10–40% 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 3.8 shows the chemical composition of hardwood tension wood (Schwerin 1958). Tension wood has lower lignin content and higher cellulose content as compared to normal wood. There is

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	10.–3.8	2.2	7.1–12.9	10.0
Glucuronarabinoxylan	–	8	–	8
Other polysaccharides	–	2	–	2

Source: Adapted from Panshin, A.J. and de Zeeuw, D. 1980. *Textbook of Wood Technology*, McGraw-Hill, New York.

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: Adapted from Schwerin, G. 1958. *Holzforschung* 12: 43–48.

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 unclear. For example, many descriptions do not describe if the samples were preextracted 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 3.14 provide summaries of various types of chemical composition of hardwoods and softwoods in the United States

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: Adapted from Moore, W. and Johnson, D. 1967. *Procedures for the Chemical Analysis of Wood and Wood Products*. USDA, Forest Service, Forest Products Laboratory.

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: Adapted from Moore, W. and Johnson, D. 1967. *Procedures for the Chemical Analysis of Wood and Wood Products*. USDA, Forest Service, Forest Products Laboratory.

and the world. These data have been collected from the analytical laboratories of the USDA, Forest Service, Forest Products Laboratory from 1927 to 1968.

3.8.1 SAMPLING PROCEDURES

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, and so on, it is critical to report these conditions along with the chemical analysis. It is also important to report the exact analytical

TABLE 3.11
Chemical Composition of North American Hardwoods and Softwoods

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

continued

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

Botanical Name	Common Name	Holo cellulose	α -cellulose	Pento sans	Klason Lignin	1% NaOH	Solubility				
							Hot Water	EtOH/Benzene	Ether	Ash	
<i>Lithocarpus densiflorus</i>	Tanoak	71.0	46.0	20.0	19.0	20.0	5.0	3.0	0.4	0.7	
<i>Melaleuca quinquenervia</i>	Cajeput	—	43.0	19.0	27.0	21.0	4.0	2.0	0.5	—	
<i>Nyssa aquatica</i>	Water tupelo	—	45.0	16.0	24.0	16.0	4.0	3.0	0.6	0.6	
<i>Nyssa sylvatica</i>	Black tupelo	72.0	45.0	17.0	27.0	15.0	3.0	2.0	0.4	0.5	
<i>Populus alba</i>	White poplar	—	52.0	23.0	16.0	20.0	4.0	5.0	0.9	—	
<i>Populus deltoides</i>	Eastern cottonwood	—	47.0	18.0	23.0	15.0	2.0	2.0	0.8	0.4	
<i>Populus tremuloides</i>	Quaking aspen	78.0	49.0	19.0	19.0	18.0	3.0	3.0	1.2	0.4	
<i>Populus trichocarpa</i>	Black cottonwood	—	49.0	19.0	21.0	18.0	3.0	3.0	0.7	0.5	
<i>Prunus serotina</i>	Black cherry	85.0	45.0	20.0	21.0	18.0	4.0	5.0	0.9	0.1	
<i>Quercus alba</i>	White oak	67.0	47.0	20.0	27.0	19.0	6.0	3.0	0.5	0.4	
<i>Quercus coccineu</i>	Scarlet oak	63.0	46.0	18.0	28.0	20.0	6.0	3.0	0.4	—	
<i>Quercus douglasii</i>	Blue oak	59.0	40.0	22.0	27.0	23.0	11.0	5.0	1.4	1.4	
<i>Quercus falcata</i>	Southern red oak	69.0	42.0	20.0	25.0	17.0	6.0	4.0	0.3	0.4	
<i>Quercus kelloggii</i>	California black oak	60.0	37.0	23.0	26.0	26.0	10.0	5.0	1.5	0.4	
<i>Quercus lobata</i>	Valley oak	70.0	43.0	19.0	19.0	23.0	5.0	7.0	1.0	0.9	
<i>Quercus lyrata</i>	Overcup oak	—	40.0	18.0	28.0	24.0	9.0	5.0	1.2	0.3	
<i>Quercus marilandica</i>	Blackjack oak	—	44.0	20.0	26.0	15.0	5.0	4.0	0.6	—	
<i>Quercus prinus</i>	Chestnut oak	76.0	47.0	19.0	24.0	21.0	7.0	5.0	0.6	0.4	
<i>Quercus rubra</i>	Northern red oak	69.0	46.0	22.0	24.0	22.0	6.0	5.0	1.2	0.4	
<i>Quercus stellata</i>	Post oak	—	41.0	18.0	24.0	21.0	8.0	4.0	0.5	1.2	
<i>Quercus velutina</i>	Black oak	71.0	48.0	20.0	24.0	18.0	6.0	5.0	0.2	0.2	
<i>Salix nigra</i>	Black willow	—	46.0	19.0	21.0	19.0	4.0	2.0	0.6	—	
<i>Tilia heterophylla</i>	Basswood	77.0	48.0	17.0	20.0	20.0	2.0	4.0	2.1	0.7	
<i>Ulmus americana</i>	American elm	73.0	50.0	17.0	22.0	16.0	3.0	2.0	0.5	0.4	
<i>Ulmus crassifolia</i>	Cedar elm	—	50.0	19.0	27.0	14.0	—	—	—	—	

		Softwoods									
<i>Abies amabilis</i>	Pacific silver fir	—	44.0	10.0	29.0	11.0	3.0	3.0	0.7	0.4	
<i>Abies balsamea</i>	Balsam fir	—	42.0	11.0	29.0	11.0	4.0	3.0	1.0	0.4	
<i>Abies concolor</i>	White fir	66.0	49.0	6.0	28.0	13.0	5.0	2.0	0.3	0.4	
<i>Abies lasiocarpa</i>	Subalpine fir	67.0	46.0	9.0	29.0	12.0	3.0	3.0	0.6	0.5	
<i>Abies procera</i>	Noble fir	61.0	43.0	9.0	29.0	10.0	2.0	3.0	0.6	0.4	
<i>Chamaecyparis thyoides</i>	Atlantic white cedar	—	41.0	9.0	33.0	16.0	3.0	6.0	2.4	—	
<i>Juniperus deppeana</i>	Alligator juniper	57.0	40.0	5.0	34.0	16.0	3.0	7.0	2.4	0.3	
<i>Larix laricina</i>	Tamarack	64.0	44.0	8.0	26.0	14.0	7.0	3.0	0.9	0.3	
<i>Larix occidentalis</i>	Western larch	65.0	48.0	9.0	27.0	16.0	6.0	2.0	0.8	0.4	
<i>Libocedrus decurrens</i>	Incense cedar	56.0	37.0	12.0	34.0	9.0	3.0	3.0	0.8	0.3	
<i>Picea engelmannii</i>	Engelmann spruce	69.0	45.0	10.0	28.0	11.0	2.0	2.0	1.1	0.2	
<i>Picea glauca</i>	White spruce	—	43.0	13.0	29.0	12.0	3.0	2.0	1.1	0.3	
<i>Picea mariana</i>	Black spruce	—	43.0	12.0	27.0	11.0	3.0	2.0	1.0	0.3	
<i>Picea sitchensis</i>	Sitka spruce	—	45.0	7.0	27.0	12.0	4.0	4.0	0.7	—	
<i>Pinus attenuata</i>	Knobcone pine	—	47.0	14.0	27.0	11.0	3.0	1.0	—	0.2	
<i>Pinus banksiana</i>	Jack pine	66.0	43.0	13.0	27.0	13.0	3.0	5.0	3.0	0.3	
<i>Pinus clausa</i>	Sand pine	—	44.0	11.0	27.0	12.0	2.0	3.0	1.0	0.4	
<i>Pinus contorta</i>	Lodgepole pine	68.0	45.0	10.0	26.0	13.0	4.0	3.0	1.6	0.3	
<i>Pinus echinata</i>	Shortleaf pine	69.0	45.0	12.0	28.0	12.0	2.0	4.0	2.9	0.4	
<i>Pinus elliotii</i>	Slash pine	64.0	46.0	11.0	27.0	13.0	3.0	4.0	3.3	0.2	
<i>Pinus monticola</i>	Western white pine	69.0	43.0	9.0	25.0	13.0	4.0	4.0	2.3	0.2	
<i>Pinus palustris</i>	Longleaf pine	—	44.0	12.0	30.0	12.0	3.0	4.0	1.4	—	
<i>Pinus ponderosa</i>	Ponderosa pine	68.0	41.0	9.0	26.0	16.0	4.0	5.0	5.5	0.5	
<i>Pinus resinosa</i>	Red pine	71.0	47.0	10.0	26.0	13.0	4.0	4.0	2.5	—	
<i>Pinus sabiniana</i>	Digger pine	—	46.0	11.0	27.0	12.0	3.0	1.0	—	0.2	
<i>Pinus strobes</i>	Eastern white pine	68.0	45.0	8.0	27.0	15.0	4.0	6.0	3.2	0.2	
<i>Pinus sylvestris</i>	Scotch or scots pine	—	47.0	11.0	28.0	—	1.0	—	1.6	0.2	
<i>Pinus taeda</i>	Loblolly pine	68.0	45.0	12.0	27.0	11.0	2.0	3.0	2.0	—	
<i>Pseudotsuga menziesii</i>	Douglas fir	66.0	45.0	8.0	27.0	13.0	4.0	4.0	1.3	0.2	

continued

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

Botanical Name	Common Name	Holocellulose	α -cellulose	Pento sans	Klason Lignin	Solubility				
						1% NaOH	Hot Water	EtOH/Benzene	Ether	Ash
<i>Sequoia sempervirens</i>	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
<i>Taxodium distichum</i>	Bald cypress	—	41.0	12.0	33.0	13.0	4.0	5.0	1.5	—
<i>Thuja occidentalis</i>	Northern white cedar	59.0	44.0	14.0	30.0	13.0	5.0	6.0	1.4	0.5
<i>Thuja plicata</i>	Western red cedar	—	38.0	9.0	32.0	21.0	11.0	14.0	2.5	0.3
<i>Tsuga canadensis</i>	Eastern hemlock	—	41.0	9.0	33.0	13.0	4.0	3.0	0.5	0.5
<i>Tsuga heterophylla</i>	Western hemlock	67.0	42.0	9.0	29.0	14.0	4.0	4.0	0.5	0.4
<i>Tsuga mertensiana</i>	Mountain hemlock	60.0	43.0	7.0	27.0	12.0	5.0	5.0	0.9	0.5

Source: Adapted from Pettersen, R.C. 1984. *The Chemistry of Solid Wood*, Advances in Chemistry Series 20, Chapter 2, pp. 57–126, Washington, DC: ACS

TABLE 3.12
Polysaccharide Content of Some North American Woods

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

continued

TABLE 3.12 (continued)
Polysaccharide Content of Some North American Woods

Scientific Name	Common Name	Glu	Xyl	Gal	Arab	Mann	Uronic	Acetyl	Lignin	Ash
<i>Pinus resinosa</i>	Red pine	42	9.3	1.8	2.4	7.4	6.0	1.2	29	0.4
<i>Pinus rigida</i>	Pitch pine	47	6.6	1.4	1.3	9.8	4.0	1.2	28	0.4
<i>Pinus strobus</i>	Eastern white pine	45	6.0	1.4	2.0	11	4.0	1.2	29	0.2
<i>Pinus sylvestris</i>	Scots pine	44	7.6	3.1	1.6	10	5.6	1.3	27	0.4
<i>Pinus taeda</i>	Loblolly pine	45	6.8	2.3	1.7	11	3.8	1.1	28	0.3
<i>Pseudotsuga menziesii</i>	Douglas-fir	44	2.8	4.7	2.7	11	2.8	0.8	32	0.4
<i>Thuja occidentalis</i>	Northern white cedar	43	10.0	1.4	1.2	8.0	4.2	1.1	31	0.2
<i>Tsugacanadensis</i>	Eastern hemlock	44	5.3	1.2	0.6	11	3.3	1.7	33	0.2

Source: Adapted from Pettersen, R.C. 1984. *The Chemistry of Solid Wood*, Advances in Chemistry Series 20, Chapter 2, pp. 57–126, Washington, DC: ACS.

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

Scientific Name	Common Name	Components of Hemicelluloses									
		Carbohydrates					Hemicelluloses				
		Cell	Total Hemi	Glucmann	AcGlu	UrXyl	Arab Gal	Pectin	Lignin	Total Ext	Ash
<i>Acer rubrum</i>	Red maple	40.7	30.4	3.5	23.5	1.6	1.9	23.3	5.3	0.3	
<i>Aesculus octandra</i>	Yellow buckeye	40.6	25.8	3.6	18.6	1.0	2.6	30.0	3.1	0.5	
<i>Carya glabra</i>	Pignut hickory	46.2	26.7	1.1	22.1	1.2	2.3	23.2	3.4	0.6	
<i>Carya illinoensis</i>	Pecan	38.7	30.2	1.6	24.7	1.6	2.3	23.2	3.4	0.6	
<i>Carya tomentosa</i>	Mockernut	43.5	27.7	1.5	21.5	1.3	3.5	23.6	5.0	0.4	
<i>Cornus florida</i>	Flowering dogwood	36.8	35.4	3.4	27.2	1.0	5.0	21.8	4.6	0.3	
<i>Fagus grandifolia</i>	American beech	36.0	29.4	2.7	23.5	1.3	1.8	30.9	3.4	0.4	
<i>Fraxinus Americana</i>	White ash	39.5	29.1	3.8	22.1	1.4	1.9	24.8	6.3	0.3	
<i>Gordonia lasianthus</i>	Loblolly-bay	43.8	29.1	4.1	22.1	1.1	1.8	21.5	5.2	—	
<i>Liquidambar styraciflua</i>	Sweetgum	40.8	30.7	3.2	21.4	1.3	4.9	22.4	5.9	0.2	
<i>Liriodendron tulipifera</i>	Yellow poplar	39.1	28.0	4.9	20.1	0.7	2.4	30.3	2.4	0.3	
<i>Magnolia virginiana</i>	Sweetbay	44.2	37.7	4.3	20.2	1.6	1.6	24.1	3.9	0.2	
<i>Nyssa aquatica</i>	Water tupelo	45.9	24.0	3.5	18.6	0.8	1.1	25.1	4.7	0.4	
<i>Nyssa sylvatica</i>	Black tupelo	42.6	27.3	3.6	18.0	1.0	4.8	26.6	2.9	0.6	
<i>Oxydendrum arboreum</i>	Sourwood	40.7	34.6	1.3	31.9	1.0	0.4	20.8	3.6	0.3	
<i>Persaeaborbonia</i>	Redbay	45.6	25.6	1.0	23.2	0.9	0.5	23.6	5.0	0.2	
<i>Platanus occidentalis</i>	Sycamore	43.0	27.2	2.3	22.3	1.4	1.2	25.3	4.4	0.1	
<i>Populus deltoids</i>	Eastern cottonwood	46.5	26.6	4.4	16.8	1.6	1.8	25.9	2.4	0.6	
<i>Quercus alba</i>	White oak	41.7	28.4	3.1	21.0	1.6	2.7	24.6	5.3	0.2	
<i>Quercus coccinea</i>	Scarlet oak	43.2	29.2	2.3	23.3	1.4	2.2	20.9	6.6	0.1	
<i>Quercus falcata</i>	Southern red oak	40.5	24.2	1.7	18.6	1.7	2.2	23.6	9.6	0.5	
<i>Quercus ilicifolia</i>	Scrub oak	37.6	27.5	1.0	22.3	1.8	2.4	26.4	8.0	0.5	
<i>Quercus marilandica</i>	Blackjack oak	33.8	28.2	2.0	21.0	2.3	2.9	30.1	6.6	1.3	
<i>Quercus nigra</i>	Water oak	41.6	34.8	3.0	28.9	2.2	0.7	19.1	4.3	0.3	
<i>Quercus prinus</i>	Chestnut oak	40.8	29.9	2.9	23.8	1.8	1.4	22.3	6.6	0.4	

continued

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

Scientific Name	Common Name	Components of Hemicelluloses									
		Carbohydrates			Hemicelluloses						
Cell	Total Hemi	Glucmann	AcGlu	UrXyl	Arab Gal	Pectin	lignin	Total Ext	Ash		
<i>Quercus rubra</i>	Northern red oak	42.2	33.1	3.3	26.6	1.6	1.6	20.2	4.4	0.2	
<i>Quercus stellata</i>	Post oak	37.7	29.9	2.6	23.0	2.0	2.3	26.1	5.8	0.5	
<i>Quercus velutina</i>	Black oak	39.6	28.4	1.9	23.2	1.1	1.9	25.3	6.3	0.5	
<i>Quercus virginiana</i>	Live oak	38.1	22.9	1.0	18.3	1.7	1.9	25.3	13.2	0.6	
<i>Sassafras albidum</i>	Sassafras	45.0	35.1	4.0	30.4	0.9	<0.1	17.4	2.4	0.2	
<i>Ulmus Americana</i>	American elm	42.6	26.9	4.6	19.9	0.8	1.6	27.8	1.9	0.8	

Source: Adapted from Pettersen, R.C. 1984. *The Chemistry of Solid Wood*, Advances in Chemistry Series 20, Chapter 2, pp. 57–126, Washington, DC: ACS. Note: Cell = Cellulose.

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

Source: Adapted from Pettersen, R.C. 1984. *The Chemistry of Solid Wood*, Advances in Chemistry Series 20, Chapter 2, pp. 57–126, Washington, DC: ACS.

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.

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 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

Wood materials = Extractives + holocellulose + lignin + inorganics (ash).

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

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, and so on, could be applied according to the nature of extractives and sample type, that is, bark, leaves, and so on.

3.8.2.2 Sample Preparation

It is highly recommended to have a fresh sample. If not, 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 h (usually at 105°C) 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.

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, mix one volume of ethanol and one volume of toluene

3.8.2.5 Procedures

Weigh 2–3 g of samples into covered preweighed extraction thimbles. Place the thimbles in a vacuum oven not exceeding 45°C for 24 h, or to a constant weight. Cool the thimbles in a desiccator for 1 h 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 h, 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 h. 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 h of successive extraction with 95% alcohol, however, two successive extractions, 4 h with ethanol followed with distilled water for 1 h 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 $575 \pm 25^\circ\text{C}$ for 3 h, 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 unknown, determine it by drying a corresponding specimen to constant weight in a vacuum oven at $105 \pm 3^\circ\text{C}$.

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 $575 \pm 25^\circ\text{C}$.

3.8.3.4 Procedure

Carefully clean the empty crucible and cover, and ignite them to constant weight in a muffle furnace at $575 \pm 25^\circ\text{C}$. 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 $575 \pm 25^\circ\text{C}$ for a period of at least 3 h, 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 suspected if they differ by more than 0.5 mg. Since the ignition temperature affects the weight of the ash, only values obtained at $575 \pm 25^\circ\text{C}$ 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, and (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 min, 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 6–8 h 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 h 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 disc glass thimble, wash with acetone, vacuum-oven dry at 105°C for 24 h, 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 α -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% NaOH.

3.8.5.2 Principle of Method

Extractive-free, lignin-free holocellulose is treated with NaOH 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 $20 \pm 0.1^\circ\text{C}$ 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 solution, NaOH, 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 entire specimen becomes soaked with the NaOH solution. After the addition of the first portion of 17.5% NaOH solution to the specimen, at 5 min 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 h 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 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 h before weighing.

3.8.5.6 Calculation and Report

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

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

where

W_2 = weight of the oven-dry α -cellulose residue, and

W_1 = weight of the original oven-dry 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-1106-84. 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 micro-filter, 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 a 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, 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.

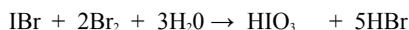
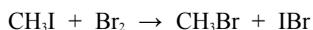
3.8.7 DETERMINATION OF METHOXYL GROUPS

3.8.7.1 Scope

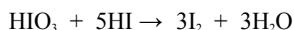
Methoxyl groups ($-\text{OCH}_3$) are present in the lignin and lignin derivatives as side chains of aromatic phenylpropanes and in the polysaccharides mainly as methoxy uronic acids. Methoxyl content is determined using ASTM, D-1166-84.

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.



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:



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 $\text{CdSO}_4 \cdot 4\text{H}_2\text{O}$ in 1 L 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 $\text{Na}_2\text{S}_2\text{O}_3 \cdot \text{H}_2\text{O}$ 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 $\text{Na}_2\text{S}_2\text{O}_3$. 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 30–45 min, 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 min 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 1–2 min. Add 10 mL of KI solution and 10 mL of H_2SO_4 , and titrate the liberated iodine with $\text{Na}_2\text{S}_2\text{O}_3$ 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 $\text{Na}_2\text{S}_2\text{O}_3$ solution required for the titration

N = normality of $\text{Na}_2\text{S}_2\text{O}_3$ solution

G = grams of moisture free sample

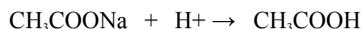
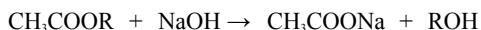
Table 3.9 shows the methoxyl content of some common hardwoods and softwoods.

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-esterification; 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.



3.8.8.2 Reagents

2% formic acid. Dilute 2 mL of 90% formic acid to 900 mL of deionized H₂O.

Internal standard stock solution: Weigh 25.18 g of 99+% propionic 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 1 N: Weigh 4 g 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 1 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 h. 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 Carbowax C/0.3% carbowax 20 M/0.1% H₃PO₄-3 ft 1/4 in. 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:

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

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

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