

PROGRESS IN THE CHEMISTRY OF LIGNIN 1943-1954

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In the 10-year period immediately before 1943 there were four discoveries that increased significantly our knowledge of the chemistry of lignin; these were, the isolation of a small amount of alcohol-soluble lignin directly from wood (1)², the discovery of small amounts of several monomeric compounds related to lignin in the ethanolysis products of wood (2), the discovery that some isolated lignins and spruce wood gave high yields of vanillin when heated at 160° with nitrobenzene and alkali (3), and the discovery that hydrogenolysis of a methanol-HCl lignin gave high yields of compounds related to 2-methoxy-4-propyl phenol (4). A handicap at that time was the lack of information on compounds that may be considered as lignin model compounds.

Prior to this period there had been considerable difference of opinion among investigators as to aromatic nature of lignin. As a result of these discoveries and ultraviolet data on lignin and wood products, a polymeric aromatic structure for lignin composed of 2-methoxy-4-propyl phenol type building blocks was accepted by most investigators. These advances plus the need for a means of utilizing lignin have stimulated many investigators to do further lignin research. These researches have been aided by several reviews of the chemistry of lignin (5, 6, 7, 8). In all these reviews the suggestions of Klason (9) that lignin is related to, if not made up of, polymers of coniferyl alcohol is acknowledged, although Klason himself had no experimental work to back up his belief. Coniferin, a glucoside of coniferyl alcohol, is present in the cambial sap of spruce and was considered as the source of lignin.

¹Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

²Underlined numbers in parentheses refer to the literature cited at the end of this report.

Distribution and Nature of Lignin

Several investigators have sought to gain further knowledge of the nature and distribution of lignin by studying plants other than wood. Suarez and coworkers (10, 11) studied the lignin in ferns and found its reaction similar to wood lignin. It could be freed from cellulose after hydrolysis by cupra-ammonium solution, dissolved by ethanol-hydrochloric acid mixtures, and the lignin reacted with sulfite solution at 125° to 135°. Vener (12) isolated lignin from a woodlike tropical fern. This lignin contained only 1 percent methoxyl. A lignin molecule having 49 carbons was found to have 2 carboxyl and 5 phenolic hydroxyl groups. This would indicate that a compound other than coniferyl alcohol was the precursor of this lignin. Lignin from grape epicarp and extracted grape seed (13) was low in methoxyl and contained pentosan. The yield of cupra-ammonium lignin was 35 to 37.9 percent.

Lignin was isolated from cork by De Baun and Nord (14). This lignin had a low methoxyl content. They found their lignin to be contaminated with extractives that would account in part for the low methoxyl values. Lignin in redwood bark is low in methoxyl and appears to be combined with the carbohydrate (15).

Some investigators (16) contend that lignin is a product of the isolation method and that lignin does not preexist in wood. Kratzl and coworkers (17, 18) reviewed the evidence for such a view and carried out experimental work to establish proof for the presence of aromatic compounds in wood. They point out that carbohydrates do not give vanillin and other aldehydes when oxidized by nitrobenzene and alkali and that aromatic compounds such as coniferyl alcohol and related compounds do. Only aromatic C₆ C₃ type compounds give propyl cyclohexanol derivatives on hydrogenolysis and phenyl propane compounds on ethanolysis. Botanical methods, including optical observations, stains, and fluorescence, showed that isolated lignin and wood sections showed the presence of similar type aromatic compounds. Ultraviolet and infrared absorptions showed the presence of aromatic compounds in both isolated lignin and in wood sections. Color reactions to phenols and aromatic amines of isolated lignin and wood sections were the same. These authors conclude that these are proof of an aromatic lignin in wood.

In opposition, Schutz and Sarten (19) found that wood gave no coloration with diazo compounds and that the product isolated from spruce wood by the action of a diazobenzene 4-sulfonic acid gave no aromatic compounds related to lignin. They conclude lignin is a decomposition product. Piettre (20) extracted a product from wood that appeared to be related to humic acid. This was thought to represent the first stage of lignin formation. In support Lange (21) found evidence for one aromatic ring for each

10 carbons in lignin on the basis of ultraviolet absorption studies of wood and lignin. Some structural changes as shown by ultraviolet were found to have occurred in the isolation of lignin by the hydrochloric acid method, but no change was found in the amount of aromatic groups. Sections of wheat straw and several woods were treated with various chemicals and then with 1 percent sodium hydroxide (22). Photomicrographs of the sections showed dark areas where some delignification had occurred. Fractional extraction of wood with delignifying agents (23) was followed microscopically. A structural change occurred during lignin removal. Ploetz (24) found that pretreatment of wood with dilute acid permits removal of cellulose by dissolving in cupra-ammonium solution or xanthation solution.

A Lignin-Carbohydrate Bond

Many of the chemical reactions of wood indicate the presence of some type of bond between lignin and carbohydrates in wood. On the other hand, some observations with the ultramicroscope on the microstructure of wood cast doubt on the possibility of a bond between lignin and carbohydrates in wood.

Further chemical experiments support evidence for a chemical bond. Supersonic vibrations (25) on lignocellulose at 300 kilocycles per second for 1 minute permit 55 percent of wood to dissolve in Schweitzer's reagent. The ultracentrifuge showed that 50 percent of that going into solution was alpha cellulose. Colloidal grinding in the presence of hydrazine dissolved lignin not soluble otherwise (26). Swelling and staining experiments (27), optical observations in sodium light and between cross nicols, and X-ray data on jute fibers show that removing the last traces of lignin causes a great increase in the swelling of the fiber.

Wacek and Schroth (28) found alkaline nitrobenzene oxidation of the part of wood that dissolved with the hemicellulose when wood was extracted with 5 percent alkali gave vanillin, syringaldehyde, and the corresponding acid. The part of wood that remained in solution when lignin was isolated by the Halse method also gave vanillin, syringaldehyde, and the corresponding acids. They conclude that a lignin-carbohydrate compound was dissolved and not recovered.

If the failure to extract lignin from wood by organic solvents were due to a masking action of the cellulose, grinding of wood should increase the amount of lignin that could be extracted. F. E. Brauns and Seiler (29) treated spruce wood in a beater with water to produce colloidal wood but there was no increase in the solubility of lignin. They concluded the failure to extract lignin from wood was not due to mechanical reasons.

Grohn (30) contends that the procedure required for isolating lignin as well as the biosynthesis of lignin indicates a lignin-carbohydrate bond. Kawamura (31, 32, 33, 34, 35, 36, 37) and coworkers have isolated a lignin-xylose derivative by means of chromatography and have established that the xylose is bound to the lignin. This indicates that lignin is bonded to the hemicellulose of wood. Harris (38) found that treatments that hydrolyze ester or acetal linkages were necessary to bring about separation of lignin from carbohydrates. Soluble products produced by chlorination of wood in carbon tetrachloride and purified by water extraction (39, 40) yielded xylose, arabinose, and galactose on hydrolysis. Stewart (41, 42) removed a lignin-carbohydrate complex from wood by heating wood in methanol at 150°.

The solid phase produced by sulfonation of wood at pH 4-6 could not be resolved to lignin and cellulose (43). These researches lead to the conclusion that lignin is combined with the hemicellulose and possibly some of the cellulose. Some type of hydrolytic reaction is required to free the lignin.

Lignin Analysis

Most analytical methods for lignin are based on the amount of residue remaining after hydrolysis. For accurate results all nonlignin extractions must be removed but none of the lignin. In the hydrolysis all carbohydrates must be converted to soluble products but no insoluble carbohydrate decomposition products formed. All lignin must be insoluble and the hydrolytic reaction should not cleave off parts of the lignin or cause polymerization and loss of water, carbon dioxide, or other parts of the molecule. In no case are all these conditions met.

Several new procedures have been examined in an attempt to develop a more satisfactory analytical method. Chlorination, oxidation, or pulping reactions make some of the lignin soluble in the usual procedure. In order to overcome this, Giertz (44) determined the amount of lignin in pulp by dissolving the pulp in 76 percent sulfuric acid and measuring the light extinction in a colorimeter. This procedure appears not to be satisfactory for wood (45). Plant material containing nitrogenous materials must be given special treatment.

A method for making the lignin determination on fresh or wet plant tissue without preliminary drying was worked on by MacDougal and Delong (46). Jensen (47) used a preliminary treatment with 38 percent hydrochloric acid to which was added concentrated sulfuric acid to cause hydrolysis. This mixture was then diluted and boiled. The effect of sulfuric acid concentrations of 64 to 80 percent on the yield of lignin from cereal straws was

studied by Adams and Castagne (48). As was the case with maple wood (49), the minimum yield of lignin from straw with the maximum methoxyl was obtained with 72 percent sulfuric acid.

A titration method for lignin was developed by Seuzyu (50) in which lignin was chlorinated to make it soluble in sulfite solution. The lignin was then precipitated by an amine and the excess amine determined by titration. Ethylene-oxide lignin (51) plus the alkali-soluble lignin gave satisfactory lignin values. Kurschner and others (52) studied the possibility of determining the methanol produced by the action of 82 percent sulfuric acid at 200° C. as a means of lignin analysis. A modified Tingle method was used for analysis of pulps (53) in which the pulp was dissolved in a mixture of concentrated hydrochloric acid and sulfuric acid diluted and then treated with sodium hypochlorite. The excess of hypochlorite was determined after 10 minutes by adding potassium iodide and back-titrating with hypo. Keller and Borlew (54) studied the relation between chlorine number and lignin content of high-yield kraft pulps in an attempt to develop an analytical method. Thacker (55) attempted to develop a procedure for removing all extractives before hydrolysis with sulfuric acid.

Lignin from unextracted or partially extracted wood contains extractives or derivatives of extractives found in original wood (56, 57, 58, 59). Some of these extractives are polymerized by acids and appear in the lignin residue.

Some lignin is removed by the solvents used for removing extractives from wood (60, 61) and by water extraction (62, 63, 64). This water-soluble lignin gives all the reactions of the insoluble lignin. Some lignin is soluble in the acid solution used for hydrolysis (65). Lignin that has been subjected to chemical treatment, such as chlorination in the preparation of holocellulose (66, 67, 68) or isolation by a method that puts lignin in solution (69, 70, 71, 72), is more soluble in acid solution and does not give proper lignin values in the lignin determination.

Isolation of Lignin

Soluble Lignins

Lignin isolated by the method of Brauns (60) has been examined for homogeneity. Hess (73) subjected spruce alcohol-soluble lignin to fractional precipitation from a dioxane solution into benzene. The molecular weight by osmotic pressure methods ranged from 2,800 to 6,700, the methoxyl content ranged from 14.1 to 15.7 percent, and carbon content from 61.78 to 67.27 percent.

Chromatographic separation (74) of an alcohol-soluble lignin from black-wattle wood showed it to contain dark tanninlike compounds, a yellow fluorescent substance, and an almost-white lignin compound.

Nord and coworkers (75, 76, 77, 78, 79, 80) found that the yield of alcohol-soluble lignin was increased if wood or other plant substances were subjected to the action of wood-destroying organisms, such as brown rot. This liberated lignin gave the same color reactions as wood lignin and yielded aromatic aldehydes when oxidized by nitrobenzene and alkali (81). Apenitis, Erdtman, and Leopold (82) found that brown rot acted to demethylate and depolymerize lignin.

Organo-sol Lignin

Lignin is converted to an organo-soluble compound when treated with various organic solvents in the presence of a mineral acid or some catalyst.

Isolation of Lignin by Acetic Acid

Spruce wood was treated with acetic acid in the presence of magnesium chloride; 11.5 to 18 percent of the wood dissolved as a crude acetic acid lignin in three successive treatments (83, 84). The product contained 9.4 to 11.6 acetyl. When correction was made for the acetyl, the methoxyl content was 14.1 to 14.6 percent, hydroxyl content was 12.3 percent, and phenolic, 2.1 percent. Oxidation with nitrobenzene and alkali gave 10.9 percent vanillin as compared with 23 percent vanillin from cupra-ammonium lignin and about 27 percent from the lignin in untreated wood. Pauly (85) prepared acetic-acid-lignin by heating spruce wood with acetic acid containing 0.3 percent sulfuric acid. The product was soluble in chloroform and acetic acid and had molecular weights of 898 and 1,790.

Bell and Wright (86, 87) prepared acetic-acid-lignin from birch by heating birch wood with acetic acid. The water insoluble product was 25 to 29 percent of the wood and contained 17.4 percent methoxyl. The chloroform-soluble fraction of the lignin contained about 21 percent methoxyl. Fisher (88) found the reaction of acetic acid with lignin in cornstalks to be aided by the presence of hydrogen chloride.

Isolation of Lignin by Methanol and Ethanol

A study of the isolation of lignin from wood by the use of methanol or ethanol in the presence of hydrogen chloride has been continued. Schuerch

(89, 90, 91) found that the amount of lignin extracted depended on the solubility of lignin in the extracting media. Addition of chloroform or dioxane increased the lignin extracted. Wacek and Hlava (92) found that lignin isolated by methanol or ethanol and hydrogen chloride had less carboxyl and less terminal methyl groups than lignin isolated by organic solvents, such as dioxane, acetone, or methyl ethyl ketone. Lignin was isolated from Eucalyptus regnans (93) by heating with methanol for 148 hours and then with fresh methanol for 16 hours. The reaction was similar to a hydrolysis reaction. Fully methylated spruce wood when treated with methanol and hydrogen chloride (94) gave a methanol-lignin with 30.6 percent methoxyl.

An ethanol-lignin was isolated by Guillemonat and Traynard (95) and compared with a product obtained by extracting wood with cold ethanol. Analytical values did not agree. Hibbert and coworkers (96) carried out extensive work on the ethanolysis of wood with ethanol and hydrogen chloride with special study of the products that dissolved but were not precipitated by water. They found ethanolysis of maple wood and reethanolysis of ethanol-lignin gave the same low molecular weight depolymerization products (97) that were identified as 4-hydroxy-3-methoxy phenyl propanone and 4-hydroxy 3, 5-dimethoxy phenyl-propanone derivatives (98). These products were synthesized and derivatives made (99, 100). Spruce wood gave only the 4-hydroxy-3-methoxy phenyl propanone and its derivatives (101). They conclude these products came from lignin progenitors (102). The products from maple wood represented 9.8 percent of the lignin (103).

Holmberg (104) did not find the propiovanillone products from spruce reported by Hibbert and coworkers but did find many sugar derivatives. The lignin remaining in the wood after ethanolysis reacted with thio-glycollic acid in a manner similar to that in original wood. Gustafsson and coworkers (105) isolated an ethanolysis product from birch wood believed to be a dimer of syringyl glycerol.

Hagglund and Richtzenhain (106) subjected wood, various isolated lignins, and methylated lignins to ethanolysis. The yield of water-soluble oils was 10 to 13 percent from the various lignins except lignin isolated by a mixture of hydrochloric and phosphoric acids. Merewether (107) isolated 86 percent of the original lignin in Eucalyptus regnans by ethanolysis; it had a molecular weight of 1,400 after purification and contained 2 ethoxy and 9 methoxy groups. Acid hydrolysis of this lignin removed ethoxy groups (108). Alkali lignin from E. regnans was ethylated by ethanolysis treatment giving a product with 24 percent alkoxyl calculated as methoxyl (109).

Lignin has been isolated from wood as an organo-sol-lignin by the use of many different organic substances. Sawdust of quebracho was extracted with ethyl-acetoacetate yielding 23.8 percent lignin with 16.01 percent

methoxyl (110). Lignin was extracted from spruce wood by chloral hydrate yielding 22.4 percent of a chloral derivative (111). Acetonitrile, acetoxime, and acetamide extracted lignin from wood (112). Phenol and hydrochloric acid reacted with lignin to produce a soluble product in which ortho condensation to the phenol occurred (113). Thiophenol reacts in a similar manner (114). Freudenberg (115) showed that lignin could be extracted by dioxane and hydrogen chloride or tetrahydrofuran and hydrogen chloride from wood swollen by water. Lignin dissolves when wood chips are heated with triethylene glycol at 125° in the presence of aluminum chloride (116). Ethylene oxide (117, 118), in the presence of 5 percent sulfuric acid reacts with wood lignin to form a soluble product. Ethylene glycol containing hydrogen chloride extracts lignin and leaves a cellulose pulp (119). The presence of water decreases the delignifying action (120). Gillet and Urlings (121) studied the delignifying action of three neutral solvents and found higher temperatures favor greater delignification. Nine consecutive cooks at 158° with a 1:1 mixture of butanol and water removed 92.6 percent of the original lignin from aspen wood (122).

Isolation of Lignin by Thioglycolic Acid

Holmberg and Gralen (123) produced a soluble lignin by treating wood with thioglycolic acid. They interpreted the reaction as being similar to the reaction of lignin with sodium bisulfite. Three treatments were required for delignification (124). Thioglycolic acid and hydrogen chloride extract a lignin from spruce with 12.6 percent methoxyl (125). Fully methylated glycol spruce lignin gives a derivative with 25.5 percent methoxyl. Thiohydracrylic acid appears to react more rapidly than the thioglycolic acid (126, 127, 128).

Isolation by Hydrogen Sulfide and Hydrosulfide

Hydrogen sulfide and sodium sulfide react with wood to produce a soluble lignin (129) with sulfur contents ranging from 4 to 17.5 percent. Water appears to be split off in the reaction (130). Some depolymerization occurs and distillable products are formed (131). The yield of thio-lignin is not increased by colloid milling of wood or by swelling agents (132). Monoethanolamine is a solubilizing agent (133). Previous methylation of wood almost completely inhibits formation of thio-lignin (134), which would indicate the reaction takes place through a hydroxy group (135). Some monomolecular degradation products are produced during the production of thio-lignin from aspen (136). Several derivatives (137) of thio-lignin from *Eucalyptus regnans* show its building blocks to contain 9 methoxyls, 1 sulfur, 1 enolic hydroxyl group, 1 phenolic group, 3 secondary and 1 tertiary hydroxyls. Oxidation of the thio-lignin after methylation gives veratric,

isohemipenic, and veratroylformic acids (138). Molecular weight fractionation shows thio-lignin to be a mixture of two main products, one with a molecular weight between 400 and 500 and another between 1,000 and 1,500. Carboxy groups increase with increase in time of cooking and with temperature; total hydroxyl and sulfur content are almost constant (139).

Isolation of Lignin by Alkali

Further study has been made of the isolation of lignin by alkali. Polya and Vallance (140) found that lignin precipitated from alkali pulping liquors and subjected to the usual sulfuric acid method for lignin determination yielded only 89 percent insoluble lignin with 14.5 percent methoxyl. Alkali lignin from Eucalyptus regnans (141) had an equivalent weight of 863 and contained 24.7 percent methoxyl. It contained phenolic and alcoholic hydroxyl groups and was acetylated, benzoylated, and methylated, showing the presence of 8 hydroxyl groups. The lignin could be separated into an ether-insoluble fraction and an ether-soluble fraction by precipitation from dioxane (142). A study of the lignin dissolved by alkali from beech wood at 100° C. showed that 35.5 percent was dissolved in 2 hours by 8 percent sodium hydroxide as compared with only 15 percent by 4 percent sodium hydroxide in 48 hours and 21.2 percent by 24 percent sodium hydroxide in 48 hours (143).

Isolation of Lignin by Nitric Acid

A method has been developed for delignifying hardwoods by the use of dilute, spent nitric acid. Pulp yields were 38.8 percent of a high alpha pulp suitable for rayons and film (144). Many of the variables in nitric acid pulping were studied by Shinra and Tze (145), who also made a study of the lignin recovered from the process. Lieser and Schaack (146) nitrated spruce wood with a mixture of sulfuric and nitric acids. Nitro-lignin was dissolved from the nitration mixture by methanol. Removal of the methanol left a light brown residue with 10 percent nitrogen.

Hachihama (147) prepared a nitro-lignin by the action of 10 percent nitric on rice straw for 30 minutes at 50° C. The lignin was methylated, then oxidized to yield a product free from methoxyl groups. Traynard and Robert (148, 149) prepared a nitro-lignin that they subjected to various treatments. They found the product had a molecular weight of about 1,150, and contained 3NO₂, 4 COOH, 2 CO, 2 MeO, 2 phenolic OH groups. Reduction (150) with tin and hydrochloric acid gave no NH₂ groups. Freudenberg, Lautsch, and Piazzolo (151) nitrated an acetylated hydrochloric acid spruce lignin with nitrogen pentoxide. The product contained 0.9 nitro groups per C₁₀ and was insoluble in organic solvents and sodium bicarbonate. They conclude the product must be aromatic.

Isolation of Lignin by Sulfite Solutions

Considerable progress has been made in the chemistry of the sulfonation of lignin and in the chemistry of the product. Erdtman (152) found that the sulfonation of lignin was a two-stage process, one involved the sulfonation of the lignin without producing a soluble product and the other a hydrolysis-solubilizing step. At low pH both steps occurred simultaneously. At a pH of 4 to 6 only the sulfonation stage occurred, giving about 65 percent yield of what Erdtman called a "low sulfonated lignin." Subsequent treatment with 0.3 percent hydrochloric acid converted the solid to the soluble form. The low sulfonated lignin contained about 1 sulfur for 40 carbons or 4 methoxyls. About 33 percent of the lignin dissolved when sulfonated at pH 5.25 and had a ratio of 1 sulfur to 2 to 3 methoxyls (153). Further sulfonation of the insoluble lignin increased the ratio to 1 sulfur for 1 to 1.4 methoxyls (154, 155). If the "low sulfonated lignin" is refluxed with ethanol, some ethylation occurs. Resulfonation at low acidity does not remove ethoxy groups, but at high acidity ethoxy groups are replaced by sulfonic acid groups (156).

Birch and a grass, when sulfonated at pH 4-7, react more slowly, indicating a lower content of sulfonatable groups (157). Lindgren concluded that two different types of linkages were involved in the two types of sulfonation. It is proposed that most of the sulfonation follows a reaction involving a benzyl-alcohol type hydroxyl at pH 6-7 and ether groups at lower pH levels (158). More work on the identity of these groupings has been done by Mikawa and coworkers (159, 160) who used the reaction of lignin with hydrogen sulfide and phloroglucinol as a means of identifying the groups.

The kinetics of the first stage sulfonation were studied by Nokihara (161). The hydrolysis stage appears to be the rate-limiting reaction (162). If sulfonation of lignin occurs before hydrolysis, there is less damage to the cellulose (163) and lignin (164). Freudenberg, Lautsch, and Piazzolo (165) found that high pH gave a lignin with 1 sulfur for 2 methoxyls. Further sulfonation does not increase the phenol hydroxyl, indicating an ether ring but not the furane ring may be split. Lange (166) examined wood, after various periods of cooking, under the microscope and by ultraviolet absorption. He concluded that sulfonation did not change the degree of unsaturation and that it was doubtful if a coumarane ring is cleaved by sulfonation.

Beech wood that had been prehydrolyzed, preferably by sulfur dioxide, was delignified by cooking with magnesium or sodium sulfite at pH 5-7 for 8 hours (167). Alkali lignin was sulfonated at pH 8.6 (168), but the sulfonic group was split off again by heating with alkali at 160° C. Richter and Pancoast (169) in an extensive study have recently repeated a great deal of the experimental work on the sulfonation of lignin and delignification of several species of wood and have confirmed the various findings.

Properties of Lignosulfonic Acid.--Lignosulfonic acid was precipitated from technical sulfite waste liquors by 4, 4 bisdimethyl amino diphenyl methane sulfate, brucine sulfate, and lead acetate (170). Recovery was poor but the products were similar, having about 1 sulfur for 2 methoxyl groups. Precipitated lignosulfonic acid was methylated by diazomethane (171). One methoxyl was introduced for each sulfite group, giving an ether-insoluble compound with 21.7 percent methoxyl and 7.85 percent sulfur acid and an ether-soluble compound with 23.1 percent methoxyl and 10.8 percent sulfur. Lignosulfonic acids were precipitated by fluosilicic acid, giving a product with 48 to 60 percent carbon and 14.8 to 16 percent methoxyl (172). Ligninsulfonate from fermented waste pulping liquor was converted to the ammonium salt by ammonium carbonate and then treated with ammonium thiocyanate and bromine or chlorine at 0°-15° and then added to butyl alcohol to precipitate (173). The properties of the product indicate that thiocyanate had been substituted for a hydrogen in the aromatic ring.

Lignosulfonic acid precipitated from aspen pulping liquor contained 21 percent methoxyl (174). The methoxyl recovered represented 60 percent of the total in the wood. Attempts to prepare a sulfur-free product resulted in the loss of most of the methoxyl. Lignosulfonic acids from a "soft" commercial cook and from a "medium hard" laboratory cook (175) were compared by precipitation with benzacridine. The first to precipitate was lower in sulfur and gave a lower yield of vanillin on oxidation with nitrobenzene and alkali. Analysis showed that about 10 percent of the methoxyl in spruce wood was not a part of the lignin. Beta-lignin sulfonic acid (176) (the soluble lignosulfonic acid produced by cooking spruce wood at a high pH) has a higher sulfur content and gives higher yields of vanillin (33 to 38 percent) on nitrobenzene-alkali oxidation than the insoluble product.

Lignosulfonic acids having an apparent molecular weight of less than 2,000 have been separated from waste commercial pulping liquors by dialysis (177) in 65 to 80 percent purity (178). Alkaline hydrolysis of the product caused an increase of 0.67 hydroxyl for each methoxyl group and also caused an increase in molecular weight.

An ammonium lignosulfonate was deionized and converted to a barium salt (179). This was precipitated in three fractions by adding acetone. The middle and last fractions were subjected to diffusion analysis. This product showed molecular weights from 1,500 to 20,000 (180).

A barium salt of lignosulfonic acid that had been purified by dialysis was fractionally precipitated from water by ethanol. When these fractions were

calculated on a sulfur- and ash-free basis, composition was nearly uniform. Ultraviolet absorption spectra of the fractions was nearly uniform (181). Molecular weight determinations of lignosulfonic acid by Schwabe and Hasner (182) showed molecular weights ranging from 1,865 to 6,660 depending on concentration and purity. Using a shape factor of 4.6, Ivarsson (183) calculated a molecular weight of about 8,000 for lignosulfonic acid. Resulfonation caused some lowering of molecular weight.

Melander (184) prepared sodium, potassium, and ammonium salts of lignosulfonic acid by mixing the calcium salt with the sulfates of the various salts, filtering off the calcium sulfate, and evaporating in the presence of sulfur dioxide. Methoxy derivatives of lignosulfonic acid were made with diazomethane and with dimethyl sulfate (185). Attempts to desulfonate lignosulfonic acid gave a product with lower methoxyl and hydroxyl content than alkali lignin from the same wood (186).

Isolation of Lignin by Hydrotropic Solvents

Heating of wood with about 10 times its weight of a concentrated solution of sodium xylene sulfonate causes lignin to dissolve (187). The solubility of the lignin increases as the concentration of the sulfonate increases above 20 percent. A 35 percent solution of the sulfonate yields a crude pulp in 48 to 50 percent yield in 5-6 hours at 150° (188). Lignin is precipitated by diluting the recovered cooking liquor to 5 percent sulfonate. Advantage in yield and cost of chemicals over kraft pulping is claimed (189).

Isolation of Insoluble Lignin

Concentrated hydrochloric acid and 72 percent sulfuric acid are used for analytical determinations of lignin. They are also used to produce lignin for comparison with that produced by other processes, although it is recognized that the values for lignin are subject to limitations and that some changes may have occurred in the lignin during the isolation. It is recognized that low lignin values and high methoxyl content for the lignin represent most closely the true lignin content. The work of Sherrard and Harris (190), in which a series of acid concentrations were used and the methoxyl content of the lignin determined, has been repeated and confirmed by Wacek and coworkers (191, 192). A minimum value for lignin from extractive-free wood was found. This product contained the highest methoxyl content, somewhat higher than that reported by other investigators (193) who did not determine the yield and methoxyl content in the same manner. Lignin in wood that has been subjected to chlorination or oxidation is not quantitatively converted to insoluble lignin by strong acids (194).

Isolation of Lignin by a Periodate Method

Purvis and coworkers (195, 196) isolated lignin from wood by alternate treatments with sodium periodate at pH 4 and 20° C. and with boiling water at pH 7. Recovery of lignin was 92 to 97 percent for spruce and 75 to 78.5 percent for maple, birch, and beech. Analysis showed a carbon content of 55 to 61 percent. Reaction to ethanolysis, nitrobenzene-alkali oxidation, hydrogenation, and sulfonation was similar to that of lignin in wood.

Isolation of Lignin by Dilute Acid Hydrolysis

Wood saccharification processes (197, 198, 199, 200) leave a residue consisting principally of lignin but containing residual unhydrolyzed carbohydrate decomposition products and wood extractives. This product, while not pure, could represent a potential raw material for chemical processing.

Properties of Lignin

The properties of lignin differ with the method of isolation and with the treatment given wood before isolation. A small amount of lignin in wood is alcohol-soluble. The remainder is insoluble either in its original state or because it is attached to carbohydrates. Nord and coworkers (201) have increased the amount of soluble lignin from wood by enzyme action of wood-rotting organisms. The increase in solubility may be due to a cleavage of the carbohydrate complex or to chemical changes occurring in the lignin due to the enzyme action. Sulfonation, oxidation, chlorination, and alkali treatment make lignin more soluble. Strong acids appear to make lignin less soluble, although the ratio of soluble lignin to insoluble lignin in isolated sulfuric acid lignin is about the same as the ratio of soluble lignin to insoluble lignin in original wood.

Isolated lignin ranges in color in its solid state from a very light tan to a dark brown, depending on the method of isolation. Because of the light color of certain woods, it is assumed that lignin in its natural state is white or very light tan and that the color of lignin is due either to the presence of colored extractives or to deposits of colored carbohydrate decomposition products. Light-colored lignin forms dark-colored solutions in organic solvents or alkali. The color may be due to action of alkali on the phenolic portion of lignin or to some colored constituent. Enslin (202) has shown that lignin from black-wattle wood could be separated into a dark tanninlike constituent, a yellow fluorescent

constituent, and a colorless lignin product. Bailey (203) found lignin to consist of two or more products on the basis of solubility in methanol and acetone when extracted after impregnation on filter paper.

Ultraviolet Light Absorption by Lignin

Ultraviolet light absorption of lignin solutions and of solid lignin has been used to study nature of lignin. Lange and coworkers (204, 205, 206, 207) determined the ultraviolet absorption of alcohol-soluble lignin and, on the basis of ultraviolet absorption of spruce wood, estimated that lignin represented 27 to 30 percent of the wood. Sohn (208) concluded that the ultraviolet absorption at 280 m μ may be due to either 5- or 6-member rings. He made a study of furfural and other 5- and 6-member ring compounds and concluded that some degradation products or impurity may hide the true spectra of lignin. Bailey (209) used ultraviolet absorption to study 4 lignin fractions he had separated by chromatography. All fractions had a maximum absorption at 280 m μ and also between 220 and 240, indicating that the differences between fractions were slight.

Schubert and Nord (210) found the ultraviolet absorption of lignin that became alcohol soluble after decay to be the same as original alcohol-soluble lignins. Enkvist and Alfredsson (211) found hydrogen sulfide-lignin to give almost as high an ultraviolet absorption as lignosulfonic acid. On the basis of shifts in ultraviolet absorption, they concluded hydrogen sulfide-lignin contained 1 phenolic hydrogen for 3 phenyl propane groups. Kraft lignin contained 1 phenolic hydroxyl for 1 phenyl propane group.

Mrs. Aulin-Erdtman and coworkers (212 to 217) studied the ultraviolet absorption of lignin prepared in several different ways and also several model compounds for lignin. The presence of a para propyl-guaiacol unit is indicated. Shifts in the ultraviolet absorption with derivatives indicates the presence of conjugated bonds. The percent of phenolic hydroxyl in various lignin products is estimated on the basis of the shift of ultraviolet absorption due to alkali. Goldschmid (218, 219) has continued the work on the shift in ultraviolet absorption that occurs when lignin preparations are made alkaline. He found a ratio of 1 phenolic hydroxyl group to 2.2 guaiacyl propane groups in pine alkali lignin.

Infrared Absorption by Lignin

In recent years the infrared spectrophotometer has been used to study the infrared light absorption by lignin preparations. Jones (220, 221) observed the absorption by "native lignin" and its derivatives and found evidence of strong hydrogen bonding as characteristic of phenolic substances. Infrared absorption spectra of coniferyl alcohol, coniferyl

aldehyde, "native" spruce lignin, ammonium liginosulfonate, and methylated spruce lignin were compared with that of a dehydrogenation polymer produced by the action of an enzyme from mushroom on coniferyl alcohol. It was found that the infrared absorption of the dehydrogenation polymer resembled that of spruce lignin (222).

Kuhn (223) observed the infrared absorption of a large number of carbohydrates and their derivatives. These did not give the absorption given by lignin and by thin wood sections (224, 225). Kratzl and Tschamler (226) observed that the spectra of lignin had a similarity to aromatic derivatives of cellulose and differed from methyl cellulose and furfural polymers. Nord and coworkers (227, 228, 229) observed that the infrared spectra of enzymatically liberated lignin was similar to native lignin.

Molecular Weight of Lignin

Molecular weight determinations of lignin and lignin derivatives show that lignin preparations are a mixture of polymers with different degrees of polymerization. Schwabe and Hasner (230) found one sample of liginosulfonic acid before dialysis to have a molecular weight of 1,865 at 0.9 gram per liter concentration and 2,450 at 3 grams per liter concentration; another fraction of a dialyzed product had molecular weights from 5,180 to 6,660. Ivarsson (231) found a molecular weight of about 8,000 for liginosulfonic acid, using a shape factor of 4.6. Resulfonation of the liginosulfonic acid lowers the molecular weight.

Gralen (232) measured the molecular weight of a thioglycolic acid lignin and a hydrobromite lignin by the Svedberg ultracentrifuge. A degree of polymerization of 36 was found, or a molecular weight of about 7,000. Heating of the thioglycolic acid lignin with thioglycolic acid and hydrochloric acid or with alkali depolymerized the lignin to about half its original molecular weight. "Native" spruce lignin that had been fractionally precipitated from benzene had molecular weights of 2,800 to 6,700 when measured by osmotic pressure method (233).

Various samples of lignin were fractionally precipitated and the molecular weights of the fractions determined (234, 235). Their maxima of molecular weight were about 800, 1,200, and 1,400 to 1,700. An alkali lignin showed a portion with a molecular weight of about 400. "Rast" molecular weights of thio and alkali lignin were about 500. Methylated and acetylated derivatives of these same lignins were 1,000 and 1,500. Deacetylated acetyl-lignin again had a molecular weight of about 450. Methylation with diazomethane gave a product with molecular weights of 1,000 and 1,500. It was concluded that reactions that replace the phenol hydroxyl group gave higher molecular weights (236).

Fractionation of Lignin by Chromatography

Soluble lignin has been subjected to chromatographic separation in attempts to fractionate lignin. Bailey (237, 238, 239) found that various lignins, when placed on filter paper and treated with a solvent, separated into zones that were heterogeneous. The phenolic fraction from the alkali and "kraft" pulping of spruce wood could be separated by paper chromatography (240). Enslin (202) separated a "native" lignin into three products by using first a diatomaceous earth and then a cellulose powder in a column. Bland and Gatley (241) determined the R_f values for two components of a methanol-lignin from Eucalyptus regnans to be 0.05 and 0.95, when a mixture methanol 40 parts, isopropyl ether 80 parts, and water 20 parts was used as the developing agent.

Oak and maple alkali lignins appeared to be homogeneous when subjected to separation by electrophoresis, while "native" pine lignin appeared to contain a mixture of products (242).

Fine Structure of Lignin

Jodl (243) studied many of the physical properties of lignin. He found the interplanar spacings of cupra-ammonium lignin to be 9A. x 15A x 3.9A, the density to be 1.41, and the surface area of 1 gram of lignin to be 180 m². Water is bound by lyosorption and capillary condensation. Zahn and Lautsh (244) studied the X-ray of lignin and model compounds. They were unable to draw any conclusions as to chemical structure from their X-ray data.

Color Reactions of Lignin

Lignin and wood react with amines and phenols to produce colored compounds that are useful in determining the presence of lignin and indicate certain structures for lignin. In 1944 Schutz and Sarten (245), after studying the optical properties of wood and lignin, concluded that the formation of colored compounds was not evidence that lignin was preformed in the wood. Netien and Névoret (246) found that sulfonamides react with the lignin of wood to form a derivative that gives a strong orange-yellow color when acidified with hydrochloric acid. Moerke (247) found several amino compounds that give a color with lignin. Isolated lignins react with $SbCl_5$, $SbCl_3$, $AlCl_3$, AsI_5 to form colored addition compounds that Poggi, Serchi, and Berretti (248) designate as a "halochromic" reaction.

Adler and coworkers (249, 250) studied the color reactions model compounds and found that eugenol and methyl eugenol did not give wood-type

color reactions, but veratraldehyde, methyl coniferyl aldehyde, and coniferyl aldehyde gave color reactions. Ultraviolet absorption curves of the color developed by coniferyl aldehyde with phloroglucinol and hydrochloric acid were similar to those for native lignin. The depth of color indicated 1 coniferyl aldehyde group in lignin for 40 methoxyl and 8 carbonyl groups. Ishikawa (251) was able to extract the substance responsible for the color reaction in bamboo shoots. He assumed it to be a compound with a coniferyl-aldehyde type grouping. Seifert (252) studied the color reactions of a large number of model compounds and lignin with acetyl acetone, phloroglucinol, paraphenylenediamine, and hydrochloric acid.

A color reaction may also be used to study the effect of various reagents on wood (253). Pew (254) found that the ultraviolet absorption of the color of resorcinol on spruce lignin has the same wave length as acidified, reduced 4'7-dihydroxy 3-methoxy flavanone, the same as reduced 2', 4,4'-trihydroxy 3-methoxy chalone, and the same color as the condensation product of resorcinol and coniferyl aldehyde in acid solution. A yellow color is produced when lignin is treated with strong hydrochloric acid (255, 256) and this color is the same as that produced by 5 propenyl coniferyl aldehyde. As the reaction proceeds, the color turns to green, which is made up of a blue and a yellow. The blue color appears to be the result of condensation of the coniferyl aldehyde group with the phenyl propane of lignin in the 6 position. The group responsible for this color is destroyed by oxidation with peroxide.

Chemical Reactions of Lignin

Lignin contains many reactive groups that have been the subject of much research in the past. The hydroxyl groups of lignin readily form ethers with various alkylating agents. The nature of the hydroxyl groups may be studied by the reactivity of the ether. Brauns (257, 258) prepared alkylated lignins and submitted methylated HCl-spruce lignin to various reactions. Acetic acid with magnesium chloride, phenol, or thiophenol and hydrochloric acid cause the methylated lignin to lose 2 methoxyl groups. Heating with 5 percent sodium hydroxide at 170°-180° causes no change. Sulfuric acid (72 percent) splits off 2 methoxyl groups. Thio-glycolic acid with hydrochloric acid splits off 1 methoxyl group. On the basis of studies involving methylation of spruce wood and lignin, Freudenberg and Kraft (259) propose the formula (C_{9.93} H_{10.27} O_{3.11}) for spruce lignin.

In an attempt to prepare lignin derivatives that would be more stable and therefore more suitable for plastics and other uses, several ethers and esters were made (260, 261, 262, 263).

The reactions of lignin with hydroxyl amine were studied by Nokihara (264), who found that treatment of wood with hydroxyl amine and hydrochloric acid in ethanol solution causes 27 percent of the wood to dissolve. Two nitrogen-containing products are obtained, one with 3 methoxyls per nitrogen and the other 0.95 methoxyls per nitrogen. Lignosulfonic acid produced at high pH lost half its sulfur when treated with hydroxyl amine and hydrochloric acid. The rate of oxime reaction was determined by the rate of hydrochloric acid liberation from the amine.

Bisulfite appeared to react with the hydroxyl of lignin at high pH (265) and with both hydroxyl and some ether linkage at low pH (266). Hydrogen sulfide appeared to react with hydroxyl and phenolic ether linkages of wood (267). Nitration of wood and lignin gave a fraction of the lignin as aromatic nitro-lignin (268)

Reactions of Chlorine and Bromine

Chlorine reacts with lignin in wood and with isolated lignin to give a product in which most of the chlorines are loosely combined (269). The solubility of the lignin is increased. When wood is chlorinated in the presence of methanol, lignin becomes soluble as a chlor-lignin (270). The use of calcium carbonate to neutralize hydrochloric acid decreases the yield, indicating that hydrolysis accompanied the reaction. Mild chlorination that introduces small amounts of chlorine gives a stable chlorine derivative, while extensive chlorination yields chlorine derivatives from which the chlorine is easily lost (271). Commercial wood-hydrolysis lignin was chlorinated (272). As long as the chlorine content was below 25 to 27 percent, no methoxyl was lost. More chlorination removed methoxyl. It appears that chlorination reactions are largely by substitution.

Bromination of various isolated lignins in carbon tetrachloride gave products with about two bromines for each C_{10} of the lignin. Half of this bromine is split off by 10 percent potassium hydroxide (273). Bromination of lignin model compounds, such as propioguuaiacone in chloroform gave the 5-brom derivative, which on degradation yielded 5-brom vanillic acid (274). Bromination of lignosulfonic acid gave a soluble product that contained no sulfur and an insoluble product with 40 percent bromine. Bromination of lignosulfonic acid and several model compounds in alkaline solution yielded bromoform as a result of cleavage of side chains (275). When n-bromsuccinimide is the brominating agent, a product with 1 bromine per methoxyl is produced (276). Derivatives indicate that substitution was in the 5 position of the phenol ring. Sodium hypo bromite gives a bromine derivative of lignin when allowed to react with spruce wood (277). This derivative loses two-thirds of its bromine on treatment with 1 normal sodium hydroxide.

Reaction with Phenol and Thiophenol

Phenol (278) and thiophenol (279) react with lignin in wood or isolated lignin in presence of hydrochloric acid to give a mixture of condensation products. Oxidation of the resulting products with nitrobenzene and alkali gives products with substitution in the ortho position, indicating that the phenol condenses with the lignin in the ortho position.

A study of the rate of reaction of phenol with lignin and model compounds gave an energy of activation for the reaction of phenol with lignin of 8-10 kilogram calories.

Other products also condense with lignin. Amino and nitro-butanol react to give compounds with 1.4-1.9 percent nitrogen (280). Maleic acid reacts to give compounds soluble in alkali (281), indicating the presence of unsaturated linkages. Maleic and succinic anhydrides react with wood to give an alkali-soluble lignin product and a pulp with less than 1 percent lignin (282).

Oxidation Products of Lignin

Extensive work on oxidation and degradation by oxidation has been carried out in the past 10 years. When oxygen is used as the oxidizing agent, the amount of oxygen absorbed is proportional to the alkali present (283). Oxidation of model compounds by gaseous oxygen indicates that the ring opens between the hydroxyl groups (284). Electrolytic oxidation of butanol-lignin at a lead cathode gave ketones, acetic and oxalic acid, and substituted aromatic acids (285). Oxidation of various lignins with potassium permanganate gave veratric acid, dehydroveratric acid, isohemipinic acid, succinic acid, and metahemipinic acid (286, 287, 288), showing that lignin contains guaiacyl propane units with substitutions in both the 5 and 6 positions.

Oxidation of spruce or maple "native" lignin by chromic acid gave very little acetic acid, indicating no appreciable amount of end-methyl groups. Ethanol lignin gave 1 acetic acid for 4 to 5 C_6O_3 units. Re-ethanolysis increases the number of end-methyl groups by intramolecular changes (289). Mild oxidation of coumarones and methylated-ethanol-spruce lignin with chromic acid gave similar products and lead Wacek and Limontschew (290) to conclude that lignin contains a coumarone nucleus. Oxidation of hydrochloric acid lignin and vanillin (291) with 20 percent hydrogen peroxide yielded many of the same products, indicating similar fundamental structure. The action of sodium peroxide on spruce wood gives a light-colored product without much change in composition (292). Extractives and lignin account for most of consumption of peroxide. Methylation of spruce wood decreases sodium peroxide consumption.

When fir wood is treated for a short time with 10 percent peracetic acid, most of the lignin dissolves, leaving a pulp. The solution yields lignin products low in methoxyl groups (293). Oxidation of lignosulfonic acid (294) and of lignin (295) with metaperiodic acid required 1 mole of the acid for 195 to 200 grams of lignin. Two to 3 moles of hypochlorite react with cold hydrochloric acid lignin, and 7 moles of hypochlorite react at 95° C. Lignin sulfonate at 95° C reacts with 10-15 moles of hypochlorite (296). The reaction causes a change in the ultraviolet absorption curve. Methylation of the lignin decreases the moles of hypochlorite used. When semichemical pulps are treated with chlorine followed by sodium hydroxide and with hypochlorite, most of the lignin and some of the noncellulosic materials are removed (297). When wood is treated with sodium chlorite, lignin dissolves (298, 299) and chlorite derivatives of lignin may be recovered from the filtrate.

Oxidation of Lignin with Nitrobenzene

Most oxidation methods used for the study of lignin have been too drastic and products represent end products rather than intermediates that may be of value in determining the structure of lignin. Nitrobenzene has been used as a mild oxidizing agent for many years in reactions such as the Skraup synthesis of quinoline (300). Freudenberg and Lautsch (301) found that nitrobenzene acted as a mild oxidizing agent for lignin, giving vanillin and related compounds. Recently this work has been extended to model compounds to determine the structures that give high yields of vanillin. With the development of chromatographic methods of separation, some of the work on lignin has been repeated to determine the various products formed. Wacek and Kratzl (302) oxidized several hydroxy and keto phenyl propane compounds with nitrobenzene. Compounds with a C = O on a side chain next to the phenyl group gave acids rather than aldehydes. Compounds with a parahydroxy phenyl grouping gave higher yields of aldehydes (303).

Pearl and Lewis (304) studied the reduction of nitrobenzene by sulfite waste liquor to determine the maximum yield of products. Hibbert and coworkers (305, 306) studied the oxidizing action of nitrobenzene on many different plants to determine the yields of vanillin and syringaldehyde. They found that the ratio of products formed offered a new means of classifying plant materials. Various chemical treatments decrease the yield of vanillin (307) from lignin as follows: alkali lignin > 70 percent sulfuric acid lignin > degraded lignin > methylated lignin.

Cohen (308) reported Eucalyptus regnans yielded 4 times as much syringaldehyde as vanillin and E. marginata 1.5 times as much syringaldehyde as vanillin. Bland, Ho, and Cohen (309) separated the products of nitrobenzene oxidation of various Eucalypt woods by chromatography and were able to obtain much better separation.

Stone and Blundell (310) developed a nitrobenzene oxidation method for lignin using small samples (40 to 50 mg.). The products were separated by chromatography, extracted, and converted to a 2-4 dinitrophenyl hydrazine and then determined with a Beckman spectrophotometer. When wheat straw "native" lignin was fractionated (311), the ether-soluble fraction gave a different ratio of vanillin to syringaldehyde than the ether-insoluble fraction.

Leopold and coworkers (312, 313) conducted extensive experiments using nitrobenzene oxidation. Wood decayed by brown rot gave low yields of vanillin. When the products of the oxidation of spruce were separated chromatographically, a large number of other products, such as para-hydroxy benzaldehyde and 5-formyl vanillin, in addition to vanillin and syringaldehyde were shown to be present (314). Total yield of aldehydes recovered based on the methoxyl recovered in the aldehyde was 31 to 32 percent (315). Aldehydes from hardwoods were about 75 percent syringaldehyde. Low sulfonated lignin (316) appeared to give higher yields of vanillin based on methoxyl recovered than did wood, but this was because some nonlignin methoxyl had been lost in the preparation of the low sulfonated lignin. Soluble beta lignin sulfonic acid (317) gave higher yields of vanillin (33.0, 36.0 and 38.3 percent) as the molecular weight of the lignin decreased. Wood attacked by termites (318) left the lignin relatively unchanged and gave almost the same yield of vanillin. Methylation of lignin (319) by diazomethane, methanol and hydrochloric acid or dimethyl sulfate decreased the yield of vanillin by preventing the splitting of phenolic ether linkages in lignin. Several lignin models were condensed with resorcinol (320) and the yield of vanillin by oxidation was determined.

De Stevens and Nord determined the nitrobenzene oxidation products of bagasse lignin (321) and of "native" and enzyme-liberated lignins (322). They consider there is evidence for 1 tertiary hydroxyl, 1 alcoholic hydroxyl, 1 phenolic hydroxyl, 1 enolizable carbonyl, and 1 cyclic ether in a lignin unit.

Alkaline-nitrobenzene oxidation of lignin (323) dissolved by the chlorite process for holocellulose gave vanillin, 6-chlor vanillin, and vanillic acid; no 5-chlor vanillin was found, indicating substitution of chlorine was not in the 5 position as proposed for the action of chlorine on lignin.

Hlava and Brauns (324) concluded that the low yield of veratraldehyde when hydrochloric acid lignin and methylated hydrochloric acid lignin were oxidized was not proof that little veratraldehyde was formed, because veratraldehyde is demethylated by oxidation with nitrobenzene.

Oxidation with Metal Oxides

Pearl has used metallic oxides for the oxidation of lignin; mercuric oxide and alkali yield vanillin, acetovanillin, vanillic acid, and guaiacol (325). Calcium lignosulfonate yields the same products with mercuric oxide or silver oxide (326). Treating of kraft or sulfite waste liquor lignin with hot sodium hydroxide and mercuric oxide produces 5-(hydroxy-mercuri)-vanillin in addition to other products (327). Changing the ratio of lignin to silver oxide and of lignin to sodium hydroxide resulted in yields of vanillin ranging from 9.0 to 28.2 percent (328). The highest yield (31.4 percent) resulted with a silver oxide to lignin ratio of 3.75 and a sodium hydroxide to lignin ratio of 21.0 at 83°. A similar experiment with copper oxide gave a maximum yield at 190°. Improved separation of the products from the oxidation of sulfite waste liquor with silver oxide showed the presence of 5-carboxy vanillic acid (329) in addition to products noted before. With copper hydroxide as the oxidizing agent, 5-carboxyvanillic acid, 5-carboxy vanillin, dehydrovanillic acid, and dehydrovanillin were found in addition to other products (330). Chromatography aided in separation of products, gave recoveries up to 99 percent (331), and showed the presence of several other related compounds (332).

Cleavage of Lignin Heated with Alkali

Crude lignin heated with calcium hydroxide in 90 percent ethanol at 320° for 5 hours gave a tar fraction containing 24 percent phenols and 2.5 percent acids (333). Several isolated lignins and spruce wood yielded vanillin and acetaldehyde when heated with alkali. Sulfonated lignin gave highest yields (334). Formaldehyde also appears as a cleavage product (335). Similar experiments with model compounds indicate the formaldehyde originates in the side chain (336). The alkali-cleavable groups appear to be masked in isolated lignins. An increase in alkali concentration causes some increase in cleavage.

Heating with Hydrochloric Acid and an Alcohol

Bailey (337) found 7 low boiling compounds in 27.7 percent yield in the products resulting from the heating of butanol-lignin with 50 percent butanol containing 0.25 normal hydrochloric acid for 3 hours at 100° C. Heating of methylated spruce wood with methanol and hydrochloric acid gave a methanol lignin with 30.6 percent methoxyl, and with phenol gave a product with 3 phenol groups and 16.4 percent methoxyl (338).

Thermal Decomposition

Lignin residues from dilute acid hydrolysis of Douglas-fir wood decomposed at 375°-400° to yield a char in 55 to 66 percent yield and 5.2 to 8.9 of a settled tar. The tar was 82 percent soluble in petroleum ether and contained 35.5 percent phenolic, 32.8 percent neutral, and 7-8 percent acidic substances (339). Fractionation of the constituents of the tar yielded phenols and catechols (340). Heating of a sulfonated copper-oxide-lignin in an oil bath at 90° to 180° split off sulfur dioxide. At 250°, 69.7 percent of the sulfur was lost (341).

Cleavage by Sodium Metal in Liquid Ammonia

Lignin from various sources was 89 percent decomposed by sodium in liquid ammonia to yield 50 percent water-soluble products, 19 percent acids and phenols, 8 percent ether-soluble neutral compounds, and 11 percent high-molecular-weight substances (342). A cupra-ammonium lignin at -33° yielded monomolecular products that indicate an ether linkage was cleaved (343, 344). When the mixture of lignin and sodium in liquid ammonia was allowed to stand 7 to 8 days, the solution became colorless and the product contained an ether-soluble oil (15.7 percent) and a soluble lignin (45 percent) with 16 percent methoxyl (345).

Hydrogenation of Lignin and Wood

Work on the hydrogenation of lignin has been continued. Bailey (346) hydrogenated butanol-lignin over Raney nickel. One mole of hydrogen was absorbed by 28 grams of lignin. Several low-boiling products were identified. Stump (347) hydrogenated sulfite waste liquor, obtaining neutral compounds, phenols, and acids. Hachihama and Jodai (348, 349, 350, 351) hydrogenated wood and lignin to low-molecular-weight substances containing phenols and neutral compounds. Matsuda (352) hydrogenated lignin, obtaining a phenolic product 68.5 percent soluble in ether. Heating of lignin with cyclohexanol (353) at 300° converted some of the lignin to soluble products and some cyclohexanol to benzene. Methanol-aspen-lignin was hydrogenated over Raney nickel in water at 250° (354), producing substituted cyclohexanols, glycol derivatives, and unidentified products. Products from the hydrogenation of alkali-hardwood lignin over copper chromite at 300° to 327° contained methanol, phenolic substances, tar acid, neutral oils, and heavy oils. The phenolic fraction contained phenol, cresol, ethyl phenol, propyl phenols, and catechols (355). Wood hydrolysis residue was hydrogenated (356) to neutral oils, acids, phenols, and high-boiling products.

Lignin was hydrogenated by heating in the presence of an alcohol and sodium hydroxide (357), giving high yields of neutral compounds with a wide boiling range. Lignosulfonic acid yielded phenols at 260° C. (358). Lignin preparations heated with butanol and alkali gave catechols, monohydric phenols, and neutral oils (359, 360). Hydrogenation of wood at 150° to 225° in the presence of a small amount of alkali and a catalyst converted lignin to water- and alcohol-soluble products (361). If the reaction is interrupted at an intermediate stage, a chloroform-soluble lignin is obtained (362, 363, 364). If this soluble lignin is rehydrogenated, cyclohexanol derivatives are produced. Granath and Schuerch (365) were able to isolate a dimer of the C₁₀ lignin-building unit from this chloroform-soluble lignin. Hydrogenation of synthetic model compounds and dimers gave products similar to those obtained from lignin (366). Products from the hydrogenation of aspen wood and wheat straw (367) were separated by chromatography. Ethyl and hydroxy ethyl derivatives were found among the products. Soluble lignin obtained by mild hydrogenation of aspen was oxidized by nitrobenzene, yielding aldehydes (368). The ratio of syringaldehyde to vanillin was higher than that from wood. Hallonquist (369) hydrogenated wood under a wide range of conditions and determined the yield of low-boiling products. No products were identified.

Biological Decomposition of Lignin

An ultraviolet spectrographic method was developed for estimating the loss of lignin sulfonate by the action of fungus growth (370). Results confirm the observation that fungi decompose lignosulfonate.

Enzymes are found to decompose lignin by demethylation and by oxidation (371). Wood-rotting fungi grew on lignin as the sole source of carbon (372, 373). Fungi did not appear to use lignosulfonate but did remove it from solution (374). Residues from the action of fungi on wood resembled true lignin and contained 12.7 methoxyl (375). When wood-destroying fungi grew on alpha conidendien or vanillic acid as the sole source of carbon the products included galactose, glucose, mannose, ribose, and rhamnose (376, 377).

Fischer (378) observed that chromogenic and fluorescent groups of bacteria in soil decompose lignin in the presence of nitrogen, oxygen, and growth factors. Lignin from chestnut and acorns yielded several compounds when acted on by lignin-destroying fungi. Vanillin was among the products (379). Wood subjected to fungus attack could be molded under heat and pressure. Analysis shows a loss of methoxyl (380). Leopold (318) found that wood underwent about the same degree of decomposition in passing through the intestinal tract of a West Indian termite as in 8 months exposure to fungus attack.

Contribution of Model Compounds to the Chemistry of Lignin

Considerable progress has been made in the chemistry of compounds believed to be related to the lignin-building unit. A number of monomeric products were produced in the ethanolysis of wood. Hibbert's students have synthesized many of these and similar products and have studied their reactions. One of these, 3 hydroxy 1-(4 hydroxy 3 methoxy phenyl)-1 propanone, was methylated and ethylated; on oxidation with nitrobenzene it yielded vanillin derivatives, and on treatment with ethanol and hydrochloric acid gave a lignin-like polymer (381). The ultraviolet spectra of several ethanolysis products and related compounds indicated a relationship to 4-hydroxy 3-methoxy cinnamic aldehydes (382). The 3, 4-dimethoxy phenyl derivative was synthesized, and that too was converted to a lignin-like polymer (383). The acetyl derivatives were shown to undergo ethanolysis (384). Removal of bromine from the 1-brom-propanone and acetyl from the 1-acetyl propanone gave propanone and 1, 2-propanedione, which suggested a means of cleavage of groups in lignin (385). A triacetate was hydrolyzed to the 1, 2-propanedione (386). A 3 hydroxy 1-(4 hydroxy 3 methoxy)-2 propanone was synthesized. This was thought to be a prime lignin progenitor (387). Ethanolysis of the 3-hydroxy compound was carried out by Gardner (388).

A group of Swedish researchers have carried out extensive research on model compounds related to lignin. Model compounds form 5-brom derivatives, but lignin forms 6-brom derivatives, which may indicate the 5 position has been filled by condensation with the side chain of other groupings (389). Substituted benzyl alcohols were sulfonated to sulfonic acids. Their presence in pulping liquor inhibited sulfonation of pine heartwood (390). When there was a parahydroxy present, sulfonation and condensation with phenols was closest to that of lignin (391). Pinoresinol, which is present in extractives of wood, was sulfonated and subjected to several reactions used for lignin and found similar to lignin (392). Aromatic keto and hydroxy polyethers were oxidized by nitrobenzene and the yield of vanillin determined. They were also sulfonated. In the process ethers were changed to alcohols which react (393).

A series of substituted acetoguaiacones were sulfonated by replacing the hydroxyl group and gave amorphous sulfonic acids (394). Polymers of aromatic keto and hydroxy polyethers were 90 percent sulfonated at pH 1.7 to 1.8 (395). At 180° they were oxidized by nitrobenzene and alkali to a high yield of vanillin (396). Oxidation of polyethers proceeds by fission of ether linkages and yields products similar to lignin. If the groups are combined by carbon-to-carbon linkages, yields are low or none. Only benzyl-alcohol type alcohols or ethers give good yields of vanillin. Compounds having the hydroxy group on the beta carbon atom gave little or no vanillin (397). It was also found that parahydroxy benzyl alcohol or ether groups were sulfonated but, if the aromatic parahydroxy group was

alkylated, sulfonation was hindered (398). Dehydrogenation polymerization of coniferyl alcohol lead to the conclusion that condensation was of ether or carbon-to-carbon type. The ether-type condensation products gave good yields of vanillin; the other did not. Lignin may have both types of condensation (399).

Enkvist and Moilanen (400, 401) subjected several model substances to hydrogen sulfide and sodium hydrosulfide. Compounds such as eugenol, isoeugenol, and vanillin form only small amounts of sulfur compounds at pH 7. At 160° sodium hydrosulfide gave amorphous substances. Vanillin alcohol reacts with hydrogen sulfide to give a disulfide that resembles lignin-hydrogen sulfide compounds. Benzyl alcohol and benzyl alcohol ethers activated by a paraphenolic hydroxyl or orthohydroxyl react with hydrogen sulfide. Ether linkages are split by sodium hydrosulfide. A shift takes place and creates a new carbon-to-carbon bond.

Wacek, Kratzl and coworkers have carried out numerous researches with model compounds having 3 carbons in the side chains (402 to 413). They found that parahydroxy phenyl ethyl ketones sulfonated in the alpha and beta position to the carbonyl group. A carbonyl group in conjugation with a double bond is readily sulfonated. Ketols in 1, 3 position on a side chain react. In 1, 2 position they do not. There is little oxidation by nitrobenzene if a carbonyl group is in the beta position; if in alpha position, it reacts. A parahydroxy group increases reaction. Compounds containing the reversible aldol-type grouping split to give aldehydes. Model compounds with labeled carbon were synthesized and gave the same reactions as other lignin model compounds. They offer a further means of lignin study.

Freudenberg and coworkers have also carried on experiments with lignin model compounds (414 to 417). Compounds with hydroxy groups on a beta carbon on the 3 carbon side chain give formaldehyde when heated with alkali or mineral acids. Lignin-like polymers have been made from d-1-pinoresinol and coniferyl alcohols. Several derivatives of the polymers have been made, indicating a relationship to lignin.

Pearl (418, 419, 420) studied the reactions of vanillin and compounds related to vanillin to determine the types of derivatives that may be produced and the manner in which they are related to lignin. Zentner (421) subjected several model compounds, including propiovanillone and 2, 4-dehydroxy 3-methyl chalcone, to the action of sodium hydrosulfide for 4-5 hours at 160° C. Only the compounds with hydroxyls reacted to give sulfur derivatives. A small amount of demethylation occurred. Pew (422, 423) studied the color reactions of several model compounds and found that some derivatives of flavanones and coniferyl aldehyde gave the same color as native lignin.

Structure of Lignin

Many proposals have been made for a structure for lignin. Most of these proposals are lacking in some respect. Lignin readily undergoes polymerization and condensation in the presence of most of the reagents used for its isolation and, therefore, there is no certainty that the material studied is the same as that in wood. Studies on lignin in whole wood substance are limited because of the masking action of other wood constituents.

On the basis of a study of the residual substance from the chlorite decomposition of wood, a carbohydrate guaiacyl complex structure has been proposed (424). Freudenberg and coworkers (425 to 429) carried out extensive work to determine the various reactive groups in lignin and concluded lignin is a polymer of coniferyl alcohol; and for each C₉ in spruce there are 0.34 primary hydroxyl groups, 0.34 secondary hydroxyl groups, 0.26 phenolic hydroxyl groups, and 1.49 oxygens not in methoxyl or hydroxyl groups; 0.64 of these hydroxyl groups are phenolic ether groupings. Richtzenhain (430, 431) oxidized methylated wood and methylated lignin, obtaining aromatic compounds, some of which indicated condensation in 5 position and others in 6 position. This indicates that lignin is aromatic and condensed in the 5 and 6 positions. He contends that the splitting of ether rings does not play a part in the reaction with bisulfite, thioglycolic acid or alcoholic-hydrochloric acid solutions.

In many cases with aromatic compounds it is possible to increase the phenolic character of compounds by chlorination. Sohn (432) found the phenolic character of lignin was not increased by chlorination. Freudenberg has proposed coniferyl aldehyde as the source material for lignin, but Adler and Haggroth (433) believe some phenyl propane derivative other than coniferyl aldehyde is responsible for part of the vanillin and acetaldehyde formed from lignin on the basis of their study of the alkali treatment of lignin. A structure for lignin with alpha glyco groups has been proposed. Lindgren and Saeden (434) subjected lignin to periodate oxidation but obtained no evidence of formaldehyde which should result from a glyco oxidation. The ultraviolet absorption of several model compounds has been compared with lignin; these give evidence for an aromatic structure and also evidence for the number of aromatic groups in lignin (435).

Leopold (436) recently reviewed work on lignin chemistry and believes a guaiacyl structure for softwood lignin has been confirmed. Guaiacyl groups are connected by ether or carbon-to-carbon linkages and all or most all of the reactive groups consist of alpha hydroxy or ether groups

in the side chain activated by phenolic parahydroxy groups. Schutz, Sarten, and Meyer (437), however, do not believe that isolated lignin can be used to interpret structure because of changes occurring in isolation.

A study of model compounds has lead Kratzl (438) to believe that the formaldehyde and acetaldehyde obtained in the alkaline cleavage of lignosulfonic acid originates from side chains of aromatic compounds. Sorgato and Scipioni (439) determined the various functional groups in lignin and considered their relationship to structure. Kleinert (440) found that previous oxidation with hydrogen peroxide prevented or lessened formaldehyde formation in the alkali cleavage of lignosulfonic acid. Oxidation (441) of birch wood with hydrogen peroxide affected the copper number, but did not affect it on pine.

Several investigators have been interested in the methoxyl of wood and lignin and its relationship to structure. Wacek and coworkers (442, 443) studied the methoxyl content of wood and conclude that only 85 percent of the methoxyl is contained in isolated lignin and that a part of the remainder may be contained in a soluble lignin. Migita and Nakano (444) found that the methoxyl of lignin showed the reactivity of aromatic methoxyl. Analysis of bamboo shoots (445) at various ages indicate that methoxy groups increase and free phenolic groups increase with greater lignification. Work on other bio-methylation processes indicate methylation of lignin may occur by transmethylation (446). Merewether (447) found the methoxyl content of isolated thio-lignin higher if the wood was previously extracted with alkali.

Search for other groups in lignin has shown the presence of isobutyl groups (448). On the basis of extractives it may be expected that a safrole may be incorporated in lignin of sassafras, but the lignin did not yield piperonyl derivatives (449). A polyflavanone structure has been proposed for lignin (450). Russel (451, 452) polymerized vanillin-monoacetate to obtain a polymer that he considered identical with spruce wood lignin. The intermediate (453) of this synthesis was shown later to have a different structure than that proposed, which was not related to lignin. Goldschmid and Maranville (454, 455) found one phenolic group in 2.1 to 4.3 C₁₀ lignin units in various lignin products by an ultraviolet method based on the shift in color as compared with eugenol and conedendrin. Kurschner (456) used a nitration method and concluded that spruce contains only 8.5 percent aromatic lignin. He contends lignin in excess of this amount obtained by use of acid or alkali is formed from carbohydrates during the isolation process.

Biosynthesis of Lignin-like Substances

Polymerization of substituted phenolic compounds to amorphous products in the presence of mushroom dehydrogenase has been known for many years (457). In a study of possible synthesis of lignin in the spruce tree, Hibbert and coworkers (458) hydrogenated 2- to 3-week-old spruce buds but did not obtain propylcyclohexanols; however, 3-1/2- to 4-month-old tips did yield propylcyclohexanols. They concluded lignin must be formed by some type of polymerization later in the age of the tree.

Freudenberg and Richtzenhain (459) calculated a lignin formula on the basis of guaiacyl derivatives and assumed that the loss of phenolic hydroxyl must be due to condensation by dehydrogenation. Dehydrogenation polymerization of 5 methoxyl-pyrogallol 1, 3-dimethyl ether occurs when oxygen is passed through a solution of the compound in the presence of mushroom extract (460). In the presence of mushroom extract and air guaiacyl and syringyl compounds polymerize (461). At pH 8 polymerization of phenolic compounds in the presence of mushroom extract to an amorphous polymer was rapid (462).

In 1948, Manskaya (463, 464) published the discovery of a peroxidase in the cambial layer of conifers that caused polymerization of phenolic compounds. He found that coniferyl alcohol and vanillin were present in the cambial layer. Nord (465) observed that a methyl-paramethoxy cinnamate was formed from glucose and xylose by Lentinus lepidus and postulated its relationship to lignin and to the possibility of polymerization to lignin. Freudenberg (466, 467, 468) continued work on the dehydrogenation polymers of coniferyl alcohol which formed an amorphous polymer that reacted much as spruce lignin. Coniferin in the presence of emulsion (to hydrolyze the glucose group) gave a similar polymer by dehydrogenation polymerization (469). Methylated spruce lignin isolated by formic acid and the methylated polymer of coniferyl alcohol had similar ultraviolet absorption curves (470). Carbon content was also similar, but methoxyl and hydroxy content differed. Sinapyl and coniferyl alcohol formed copolymers by dehydrogenation in the presence of mushroom extract (471, 472). Coniferyl methyl ether also polymerized (473) and was subjected to many lignin reactions. A localized beta-glucosidase was found in the cambium that can free coniferyl alcohol so that it can react in the presence of wood peroxidase to form polymers (474, 475).

Coniferyl alcohol and 3, 4-dihydroxy cinnamyl alcohol form copolymers that have lignin-like properties. Such a polymer may account for the low methoxyl in lignin (476). Dehydrogenation polymers containing C¹⁴ have been synthesized (477, 478, 479). Formaldehyde formed by cleavage

of the product was radioactive, indicating it came from the primary (COH) grouping. Isohemipinic from the product is inactive and methemipinic is one-third active. Radioactive coniferin placed in the cambium of a tree was converted to lignin containing the entire activity (480). Pinoresinol has been isolated as a product formed by dehydrogenation polymerization of coniferyl alcohol. On further treatment pinoresinol forms an amorphous lignin-like product (481).

Baruah and Swain (482) formed an amorphous polymer from catechol in the presence of mushroom enzyme. Eugenol and hydrogen peroxide catalyzed by peroxidase formed a lignin-like amorphous polymer (483). When wheat seedlings (484) were exposed to radioactive carbon dioxide, both cellulose and lignin contained C¹⁴. Wacek, Hartel, and Maralla (485) added coniferin to spruce tissue culture in vitro but could not conclude that coniferin was converted to lignin. Formic acid and the methyl group of methionine with C¹⁴ were transferred in growing plants to methoxyl groups of lignin. The rate of transfer from methionine was 26 times faster than the rate from formic acid, indicating that methylation of lignin may be by way of methionine (486).

Utilization of Lignin

Many writers have reviewed the uses of lignin (487 to 495) for such things as tanning agents, core binders, rubber compounding agents, surface-active agents, for production of chemicals, plastics, water conditioners, for storage batteries, soil improvement, oil drilling, and protein precipitants. Prichard and Daily (496) described the use of lignin in storage batteries. Lignin may be used as a soil-stabilizing agent in road building (497, 498). Soluble lignin or insoluble lignin after being made soluble by the action of alkali and an oxidizing agent may be coprecipitated with rubber to provide reinforcing properties (499 to 506). Lignin and lignin derivatives have been tested, not too successfully, for plastics (507 to 511). Lignin has cation bonding value that make it useful for water purification. The property can be increased by condensation with various amines (512, 513). Lignin and composted sawdust have soil-building value (514 to 517). Lignosulfonic acid and its derivatives are suitable surface-active agents for producing emulsions (518 to 522). Protein may be precipitated from solution by treatment with lignin (523, 524).

Lignin under water and protected from air is very resistant to decomposition (525). Exposure to air increases rate of decomposition and the rate is increased further by the presence of algae (526). Heating of lignin with various solvents increases its activity (527).

Lignin is a source of many fine chemicals, including vanillin, that may be used for the preparation of many other chemicals. Substituted amines and ureas may be made from vanillin (528). Several derivatives were made from vanillin (529) and vanillin (530). Some of these have medicinal value (531). Vanillin may be removed from solutions from the alkaline hydrolysis of sulfite waste liquor containing as little as 0.2 percent vanillin by the use of an anion exchange resin at pH 7 (532). Vanillin may be extracted from alkaline lignin-containing liquors without acidification by tertiary butyl alcohol (533). Pearl (534) obtained vanillic acid in high yield from calcium lignosulfonate by oxidation with silver oxide in the presence of sodium hydroxide. The Ontario Paper Company (535) has developed a process for producing vanillin from sulfite waste liquor using lime instead of sodium hydroxide. The vanillin and other oxidation products are extracted by toluene. Vanillin is removed from the toluene by caustic and distilled to give a product with 97 percent vanillin.

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