THE ISOLATION AND ANALYSIS OF HEMICELLULOSES OBTAINED
FROM THE WOOD OF THE CATCLAW, ACACIA GREGGII,
BEFORE CHLORINATION

by

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The Isolation and Analysis of Hemicelluloses Obtained From the Wood of the Gatolaw, *Asaëia greggii*, Before Chlorination

INTRODUCTION

"Lignin might be defined as a compound, either aliphatic, aromatic, or heterocyclic in nature, which has a morphologic but not crystalline arrangement, which has no fusion point, which has no known inert solvent, whose reactions are obscure, whose derivatives are unexplained, whose molecular weight is decidedly uncertain, and whose fundamental chemical structure is definitely unknown. One new school of thought even denies the existence of lignin in nature, claiming it arises from chemical treatment in isolation and hence is only 'apparent'."

Lignin is found mainly in the "middle lamella" or central layer of the cell wall in "woody" tissue. It has been reported isolated from dried water hyacinth, rice straw, and the seaweeds Laminaria and Rhodymenia, though there is a question concerning the latter. An appreciable percentage of lignin was obtained by the methods involving the use of mineral acids but none by the Holmberg's thioglycolic acid method. The amount of lignin present in various plants as a function of the age has been much studied in order to determine whether pectic materials undergo transformation to lignin and whether hemicelluloses or certain groupings in these materials are converted to lignin during growth. The
main stumbling block is, of course, the fact that the chemical constitution of lignin is unknown, thereby making experimental determinations extremely difficult to devise. The theory that pectin is a precursor of lignin is based primarily on the statements that pectic materials decrease as the plant matures, accompanied by an increase in the lignin content. A more likely theory, that of the formation of lignin from the hemicelluloses, is supported at least by some indirect evidence. Buston has shown that the xylose–glucuronic acid series of the hemicelluloses are found mostly in lignified tissues, while the arabinose–galaturonic acid series appears in young tissues containing little or no lignin, thus indicating a possible qualitative relation with xylan. Furthermore, xylose and hemicelluloses containing xylose, when heated with strong acids form insoluble condensation products containing methoxyl groups which seem to be related to lignin or humins. Now there appears a possibility that lignin and polyuronide hemicelluloses are actually in chemical combination in the plant.

Another interesting statement is made by Fuchs who believes that the respiratory enzymes remove the oxygen from the carbohydrate material. Since the oxygen is given off in the form of hydrogen peroxide, the cell is in this way provided with oxygen, while in the cell wall glucal-like complexes remain.
There are various reagents which are used in the preliminary treatment of the wood. The interference of carbohydrate material has been most studied from two angles. First, it is well known that sugars, particularly arabinose, xylose, fructose, and sucrose in the presence of highly concentrated acids such as are used in some lignin determinations form insoluble humin-like materials which increase the apparent yield of lignin. However, it is a curious and unexplained fact that xylose produces more insoluble material than does arabinose. Polysaccharides containing xylose and fructose act in the same manner. Second, it is known that lignin will condense in strong acid solution with aldehyde and ketone groups to form insoluble products which are very stable to acid hydrolysis. Therefore compounds containing pentose groups may constitute a comparatively great error. The furfuraldehyde they produce under these conditions will condense readily with the lignin, or, if a small amount of lignin is present, it may itself condense to form insoluble products. Norman says that this may account for the distinct difference obtained in the apparent increase of lignin yield when small amounts of pentose are present in the determination and that of the insoluble products formed when the same amount of pentose alone is subjected to the same conditions. Two factors con-
cerning the removal of carbohydrates, then, are important: the degradation products must be soluble, and soluble fission products which might condense with the lignin should be avoided. An incorrect yield might also be obtained if hemicelluloses are present, for they are considered by some workers to be "lignin formers."

Carbohydrate materials are often removed by exhaustive extraction with hot dilute acids, 1-5 per cent., or 2 per cent. sodium hydroxide in alcohol followed by refluxing with 4 per cent. aqueous sodium hydroxide. A preliminary water extraction is said by Phillips and Goss to remove some substances which would form insoluble products in strong acid solution, and it may also remove some hemicelluloses. Some gum-like substances which are found in Eucalyptus woods are dissolved by 3-5 per cent. sodium sulfite. Harris and Mitchell state, however, that hot dilute acids, sodium bisulfite, and ammonium oxalate dissolve lignin and should be avoided. Cohen and Harris frown on all methods of mild hydrolysis. Then, there is no assurance that all these reagents other than water have no chemical effect on the lignin itself. Aronovsky and Gortner report from their work on the effects of solvents on pentose materials that mixtures of monohydroxy alcohols and water were generally less destructive toward pentosans of the wood than was water alone. The
effects of these mixtures on the pentosans increased with increasing molecular weight of the alcohols. Amyl alcohol-water mixtures caused a greater destruction of pentosans than did water alone. A pretreatment with an alcohol-benzene mixture to remove fatty and resinous substances which also increase the apparent yield of lignin is almost universally adopted now. A final washing with alcohol follows to remove any benzene which tends to be retained. Some tannins are removed by extracting in a Soxhlet apparatus with 95 per cent. alcohol for four hours.

Present methods for the determination of lignin in wood pulp are not exact and seem to depend entirely on the worker. In 1936 seven well-known chemists prepared lignin by six different methods on the identical wood pulp and two types of algae, Laminaria hyperborea and Rhodymenia palmata. The results bore out the contention of many that a practical method of preparing pure lignin is sorely needed, for there was poor agreement among these men. The method of preparing lignin most generally used depends on the use of highly concentrated acids to remove all other constituents present. Since lignified tissue varies greatly in the type and amount of extraneous material, a standard, accurate method of this sort becomes quite improbable.
Fuming hydrochloric acid, 42-43 per cent., though unpleasant with which to work, is often used. Treatment must not be prolonged to avoid alteration of the lignin; neither must it be too short or the physical and chemical unions between the lignin and carbohydrates will not be entirely destroyed and the carbohydrates will not be completely converted into forms which are soluble in water. The operation is carried out preferably at temperatures lower than ten degrees for about four hours, the low temperature being necessary to prevent the formation of reversion products which increase in amount with increase in temperature. The mixture is then diluted to about 3 per cent. acid and boiled for two hours completely to hydrolyze the cellulose and other carbohydrate material. Intermittent hydrolysis gives lower yields of lignin than continuous hydrolysis. The whole is poured into water, and the insoluble lignin filtered off. Lignin prepared in this manner is called "Willstatter lignin".

Ender and Uebel found that when spruce wood is treated with 72 per cent. sulfuric acid at temperatures between ten and forty degrees, a minimum lignin value is reached. As the temperature is increased, this value is obtained more rapidly and then is constant for quite a long period, before the time element increases the formation of humus products. They conclude that the carbohydrate material
must be entirely destroyed before the insoluble humins begin to be produced. The lignin is centrifuged out readily without dilution and hydrolysis. This is a modification of the sulfuric acid method first devised by Oat and Wilkerson which is similar to the hydrochloric acid method described previously. (20)

Recently, Freudenborg and Flotz have proposed that the name "sulfuric acid lignin" be assigned to "that wood constituent freed from sugars with sulfuric acid and having a maximum methoxyl content." The proper concentration of acid for each wood would be determined separately. Then the maximum methoxyl content is found by a series of tests using acid of different concentrations from sixty per cent up. This lower limit is essential because cellulose will not dissolve in lower concentrations. On the other hand, it was found that a too concentrated acid caused a more rapid formation of humins. It seems that the value of the lignin content passes through a minimum as the acid concentration is increased. One disadvantage in using sulfuric acid is that occasionally there are formed sulfuric acid compounds of lignin, in which form lignin may dissolve colloidal on washing. To avoid this, the lignin precipitate is heated with 0.3 per cent. hydrochloric acid for twelve hours in a sealed tube at 100 degrees, after which it is
washed with water until acid-free. The hydrochloric acid splits off the greater part of the sulfur; however, the small amount that remains is determined as ash. Another part which should be calculated as sulfur trioxide and deducted is neglected for it nearly compensates for the amount of lignin lost in the preliminary extraction with alcohol-benzene. (22)

A patent was issued in 1939 on a new rapid process using 0.4-5 per cent. sulfuric acid. The sawdust is mixed with seven to ten times its dry weight of acid, heated from 2-5 minutes at 165-380 degrees under about 90-1000 pounds pressure per square inch. Then the pressure is reduced, and the lignin filtered off in a Buchner funnel. A method based on the solubility of cellulose in a solution containing forty grams of zinc chloride, 1000 cubic centimeters of 37 per cent. hydrochloric acid and 5-10 cubic centimeters of water gave results which closely checked the values obtained by the 72 per cent. sulfuric acid and 42 per cent. hydrochloric acid methods. (23)

"Freudenberg" lignin depends on the solubility of cellulosic materials in Schweitzer's reagent. However, if the wood is not subjected to a pre-treatment with dilute agents, such as sodium hydroxide, the matter which dissolves is not cellulose, for it contains less water than cellulose; also methoxyl constituents are present. This indicates that
sodium hydroxide definitely exerts a chemical change on the wood and speaks against the view that cellulose, hemicellulose, and lignin are present as such in woods. Schweitzer's reagent has the disadvantage of introducing nitrogen which is extremely difficult to remove into both the soluble and insoluble parts of the wood.

"Meta-lignin" or "alkali lignin" is obtained by extracting the wood with 4-5 per cent. sodium hydroxide at about 160-180 degrees under considerable pressure for four to six hours. The lignin is precipitated from the dark extract by acidification. The hemicelluloses can be precipitated from this solution by adding acetone or alcohol in which the lignin is now soluble. A pre-treatment with cold, dilute sodium hydroxide to remove hemicelluloses is not very efficient and might dissolve some of the lignin. A better method is to acidify the autoclaved mixture to 2-3 per cent. acid and hydrolyze the hemicelluloses by boiling. "Alkali lignin" is fractionated into two parts; A, which is insoluble in dioxane-ether, and B, which is soluble in this solvent.

There are many methods involving the removal of lignin from wood in the form of derivatives. Industrially this process has been extensively carried out by the use of sulfurous acid or various sulfites, but lignin was the waste product. It is generally believed that the product is not homogeneous; that is, it probably contains a number of ligno-
sulfonic acids. Beta naphthylamine, basic lead acetate, and quinoline all have been used as precipitants for these acids. Recently Holmberg's method has been receiving a lot of attention, for it is said to be quantitative. By treatment of the wood with thioglycolic acid he obtained "lignothioglycolic" acids. If we designate a formula, LiOR, for lignin, a schematic equation can be set up:

\[ \text{LiOR plus } \text{HSCH}_2\text{CO}_2\text{H to give LiSCH}_2\text{CO}_2\text{H plus ROH} \]

where \( R \) may be a hydrogen atom, another lignin molecule, a fission product of lignin, or a carbohydrate residue.

Because of the fact that the two algae, Rhodymenia palmata and Laminaria hyperborea, gave 15.5 per cent lignin values by the methods involving mineral acids and none by the thioglycolic acid treatment, Schmidt-Nielsen states that most of the "lignin" obtained by the other methods is an artificial product. This is in accord with Hilpert, et al., who believe that lignin is not present in wood as such but is only a secondary reaction product.

A number of methods involving the solution of lignin by hydroxy-compounds with or without a catalyst have been extensively studied. "Methanol lignin" and "primary lignin" are prepared in this way. The wood is extracted with an alcohol-benzene mixture and then with cold 5 per cent sodium hydroxide. Then it is heated with an equal weight of 17 per cent. hydrochloric acid and ten times the weight of methyl
and ethyl alcohols respectively. After treatment for eight
to ten hours, the solution is concentrated and poured into
water acidified by hydrochloric acid. Purification is
accomplished by dissolving the precipitate in alcohol and
reprecipitating. Many other alcohols are similarly used,
the preliminary treatment with sodium hydroxide often being
omitted. After extractions with alcohol-benzene and water,
wood is refluxed with benzyl alcohol containing 5 per cent.
hydrochloric acid for one hour. The filtrate is allowed to
cool and then poured in a fine stream into a large volume
of rapidly stirring ethyl ether to precipitate the lignin.

(14)

Aronovsky and Cortner made a study of the relative
efficiencies of the various alcohols in dissolving lignin
and found that a normal butyl-water mixture is best. They
also state that the molecular structure of the alcohol has
a profound effect on its ability to pulp wood, for isopropyl,
tertiary butyl, and tertiary amyl alcohols being branched
chain alcohols behaved essentially like methanol in their
ability to remove lignin from wood. These methods cannot be
considered at all quantitative, except Holmberg's method,
for poor yields are the rule. However, Hibbert states
that his method is so mild that the hemicelluloses, pentosans,
and hexosans extracted have not been hydrolyzed. He used just
a trace of iodine or dilute hydrochloric acid for a catalyst
with no preliminary extractions. Instead of monohydroxy alcohols, glycol, glycerol, or glycerol chlorohydrin were the extracting agents.

"Phenol lignin" is prepared by slowly adding the finely divided wood to melted phenol in the presence of a catalyst, such as toluene-sulfonic acid or concentrated hydrochloric acid. After cooling, it is poured into water, and the precipitate dried and then extracted with hot alcohol in which the phenol derivative of lignin is soluble. Upon dilution with an excess of water, lignin is precipitated as a bright yellow solid. When lignin reacts with monohydroxy alcohols, glycerol, or the glycols, it is believed that only one hydroxyl group unites with a lignin molecule by an ether linkage. In the case of "phenol lignin", because of higher yields obtained, it is assumed that perhaps fifteen or twenty molecules may unite with the lignin in such a way that the phenolic hydroxy groups are free. This union is in addition to the ether linkage of one phenol molecule and one lignin molecule.

Leemmel states that his method of dissolving lignin is a quantitative one. After the sawdust is soaked in concentrated hydrochloric acid, the lignin is dissolved immediately in ethylacetocacetate without reaction or decomposition at room temperature.
Formic acid, anhydrous hydrofluoric acid, and chlorine dioxide with sodium sulfite are among other reagents which also have been used as methods of preparing lignin with no outstanding advantages and some obvious disadvantages.

A method of preparation receiving much attention now is that of Brauns. He succeeded in isolating his so-called "native lignin" with an inert solvent at room temperature. No basic or acidic catalysts were employed. Much interesting work has been done on the decomposition of cellulosic materials by bacteria, fungi, and insect larvae in an effort to isolate lignin unchanged by chemical reagents. Plotz has found that when linden wood is degraded with ethylene-diamine-copper oxide solution, the material in the wood which is precipitated by dilute acids can easily be further degraded by enzymes. A residue is always obtained in which the ratio of lignin to carbohydrate is one to one. Sixty-one per cent. of the wood, which is insoluble is the ethylene-diamine-copper oxide solution, is very difficultly attacked by enzymes, the degradation stopping when the ratio of lignin to carbohydrate becomes one to three. Therefore, he thinks that the lignin in wood is present as a carbohydrate-lignin complex, the one to three complex being the higher structural unit from which the one to one complex is derived. He actually treated the one to three complex with enzymes and
obtained a one to one complex when the reaction ceased. The enzymic degradation of native wood is much more difficult to accomplish. There are two possible explanations: "either the cellulosic or the greater part of the carbohydrate is so protected, purely mechanically, by the lignin that the enzyme cannot gain access to it, or the polysaccharides are chemically combined with the lignin component and the enzyme cannot dissolve the union". Plötz has not yet succeeded in isolating a pure lignin by this means.

Structure of Lignin

Though the structure of lignin has long been the subject of extensive research, the problem is far from being solved. Indeed, Hilpert and his colleagues believe that lignin does not have an aromatic character and even deny the existence of an original lignin. They consider it to be a reaction product of sensitive carbohydrates in the wood formed during the isolation process.

The percentage composition of lignin is very different from that of a polysaccharide. Using as a basis Brauns' native lignin, it is seen that a polysaccharide contains almost twice as much oxygen as lignin and about a third as much carbon, whereas the hydrogen content is nearly the same. That the lignin molecule can be methylated, acetylated, and benzoylated indicates the presence of hydroxyl groups. However, the degree of reactivity of the various hydroxyls
varies considerably. One group formerly believed to be an extremely active hydroxyl has recently been shown actually to be a carbonyl group. Although previously it has been assumed that methyl alcohol with hydrochloric acid as well as diazomethane introduced only one methoxyl group into the building unit of lignin, Brauns and co-workers have shown that in reality two methoxyl groups enter the molecule. The positions they take depend on the methylating agent. Brauns' "native lignin" extracted by the use of an indifferent solvent in the presence of no acidic or basic catalyst at room temperature was treated with methanol containing a little hydrochloric acid. His so-called "methanol native lignin" thus produced exhibits an increase in methoxyl content from 14.8 per cent. to 21 per cent., corresponding to two methoxyl groups per building unit. When spruce wood is treated directly with methyl alcohol and 0.5 per cent. hydrochloric acid, the same methoxyl value was obtained. An identical methoxyl content was found when Brauns' "native lignin" was methylated with diazomethane. Diazomethane methylated native lignin and methanol native lignin differ, however, in a number of ways, despite the fact that they both have two new methoxyl groups in the molecule and that they have the same methoxyl content. Diazomethane methylated native lignin is almost white and is insoluble in 5 per cent. sodium hydroxide, while methanol native lignin is a light
grey brown in color and is soluble in 5 per cent. sodium hydroxide. When diazomethane methylated native lignin is treated with 72 per cent. sulfuric acid, it is recovered unchanged, but when methanol native lignin is subjected to the same reagent, it loses two methoxyl groups. These differences indicate that in methanol native lignin, the two methoxyl groups are attached to a carbonyl group by an acetal-like linkage, and that the phenolic hydroxyl is still free, thus explaining its solubility in 5 per cent. sodium hydroxide. On the other hand, when diazomethane is used as the methylating agent, the carbonyl is no longer in the keto form, but is present as an enol group. A methoxyl group will go on this enolic group and one on the phenolic group, showing the addition of two methoxyl groups per molecule. Also the phenolic hydroxyl is not free, and this methylated lignin is not soluble in 5 per cent. sodium hydroxide.

\[
\begin{align*}
\text{Methanol native lignin} & \quad \text{Diazomethane methylated native lignin} \\
\text{CH}_3\text{O} & \quad \text{CH}_3\text{O} \\
\text{CH}_3\text{O} \quad \text{C}_4\text{H}_{32}\text{O}_2 & \quad \text{OCH}_3 \\
\text{CH}_3\text{O} & \quad \text{CH}_3\text{O} \\
\text{CH}_3\text{O} & \quad \text{C}_4\text{H}_{31}\text{O}_2
\end{align*}
\]
If this is true, then it should be and actually it was found possible to add another methoxyl group to the phenolic hydroxyl in methanol native lignin by the use of diazomethane. The value obtained, 24.4 per cent. methoxyl, was the same as that found when methanol lignin prepared by the direct action of methyl alcohol and hydrochloric acid on spruce wood was treated with diazomethane. The same product is also obtained when diazomethane methylated native lignin was treated with methanol and hydrochloric acid, although here it is not certain where the other methoxyl group attaches. The carbonyl group has been shown to be the part of the lignin molecule responsible for the purple color which develops when isolated lignin is treated with phloro-gluconol-hydrochloric acid solution, a property not characteristic of a simple alcoholic hydroxyl group. Diazomethane in ether, acting on "native lignin" gives a partially methylated product with the methoxyl group on the phenolic hydroxyl, and the carbonyl group is still capable of giving the purple color. On enolization, the product is also soluble in 5 per cent. sodium hydroxide. But when this partially methylated lignin in the enolic form is further methylated with diazomethane in dioxane solution, a methoxyl group replaces the enolic hydroxyl, and the color reaction is not evident; neither is the product soluble in 5 per cent. sodium hydroxide. Methylation with methanol-hydrochloric acid gives the product corresponding to three new methoxyl groups in the molecule,
24.4 per cent. methoxyl. In addition to the carbonyl group and the phenolic hydroxyl, there are three other hydroxyl groups which act as if they were primary or secondary alcohols of the aliphatic type. They can be methylated with di-methyl sulfate in sodium hydroxide. Therefore, when diazomethane methylated native lignin and methanol native lignin are completely methylated with basic di-methyl sulfate, the methoxyl value increases from about 21 per cent. to about 30 per cent. In general, it appears that an increase of about 5 per cent. methoxyl indicates the introduction of one methoxyl group into the building unit of lignin. Braun's native lignin when treated with thioglycolic acid in dioxane solution with a trace of hydrochloric acid as a catalyst forms a tetra thioglycolic acid lignin identical with the product obtained by Holmberg when he treated spruce wood with thioglycolic acid. Since Holmberg's method is thought to be quantitative, this reaction is significant.

Although in the literature the methoxyl content of the various lignins as isolated from the different woods fluctuates between 14 and 20 per cent., it is the one part of the lignin molecule which is widely accepted by lignin chemists. That the lignin content is a function of the age of the plant in some cases is shown by Zhorebov working with conifers and cereal plants at different stages of growth. This increase with maturity may account in part for the difference in reported results. Probably the most accurate value is that
obtained by Brauns (14.6 per cent.), because his "native lignin" was prepared without the use of drastic reagents. As we have seen, lignin as it occurs in nature and as it is prepared, is not completely methylated. The methoxy content can be raised to as high as 50 per cent. Though many workers believe that the methoxy groups in lignin are very stable because there is relatively little discrepancy in values obtained by various strenuous extracting reagents, Hilpert (46) and Meybier (40) found that the methoxy content changed from 15 per cent. to 11 per cent. when spruce lignin was boiled with hydrochloric acid. However, it is a generally accepted idea that the stability of the methoxy groups indicates an ether linkage of the methoxy to the building unit.

Demethylation of lignin has not been extensively studied. (41) As noted above, Hilpert and co-workers have shown that the methoxy groups are somewhat sensitive to hot dilute acids. (6) Because the demethylation occurs in stages according to the reagents used suggests that all the methoxys are not of the same general nature. Dry chlorine in carbon tetrachloride removes some of them, chlorine in the presence of water more methoxy groups; then a part cannot be removed even in a basic solution—optimum conditions for demethylation with chlorine. Lignin treated in this manner cannot be remethylated; thus showing that secondary changes undoubtedly have taken place.
Hibbert, Brauns, and co-workers recently suggested a "building unit" for lignin with a molecular weight of about 840. This "building unit" consists of five so-called "building stones" or C6-C3 groups with a molecular weight of around 170. This C6-C3 grouping and the "building unit" have been substantiated by numerous other workers, including Hagglund, Holmberg, and Freudenberg. Brauns uses the analogy that the lignin "building stone" and the lignin "building unit" are related to lignin in the same way as glucose is the building stone of cellulose and starch, whereas cellobiose and maltose are their respective "building units". It has long been believed that lignin is related to coniferin, a glucoside which hydrolyses to give coniferyl alcohol.

Coniferyl alcohol contains this basic C6-C3 grouping and can be oxidized to give vanillin.

Lignosulfonic acids upon heating under pressure with nitrobenzene and sodium hydroxide were also shown to produce small amounts of vanillin. However, until recently it was believed that vanillin could not be obtained with these reagents unless the sulfonic acid of lignin was used and unless the sulfonic acid group itself was adjacent to the vanillin group. Freudenberg succeeded in isolating a 25 per cent. yield of vanillin by treating spruce wood in this manner. He also found relatively large amounts of vanillin when isolated Freudenberg and Willstatter lignins were subjected to the same treatment.
This experiment is considered important, because it helps to indicate the fundamental aromatic structure of lignin. Further evidence for this theory is presented by Hatihama, Zyodai, and Umezuk who found dihydroeugenol in large amounts by the hydrogenation of softwood lignin in a dioxane solution using nickel oxide as a catalyst. Harris and Adkins by catalytic hydrogenation of lignin under pressure with copper-chromite as a catalytic agent found propyl-cyclohexane derivatives. Adkins, Frank, and Bloom think that with this method the hydrogen cleaves the bond between the propyl benzene groups (or related groups) which are joined in chains. The recurrence of the C₆-C₃ group is to be noted in this whole discussion for, although workers differ as to the true "building stone" of lignin, nearly all the proposed groups can be reduced to this basic C₆-C₃ group.

Ligninsulfonic acids of various woods have been ex-
(52,53,54) tensively studied in this connection. Upon treatment of these acids with hot aqueous alkali, a number of products have been obtained, including vanillin acetovanillone, syringaldehyde, and acetosyringone.

\[ \text{Acetovanillone} \]

\[ \text{Syringaldehyde} \]

\[ \text{Acetosyringone} \]
Spruce wood treated with absolute alcohol containing 3 per cent. hydrochloric acid for forty hours yielded a phenolic substance whose methyl ether was shown by synthesis to be alphaethoxy propioveratrone.

Therefore, it is believed by Cramer, Hunter and Hibbert that alpha hydroxypropioveratrone or a dismutation isomer is the true "building stone" of lignin. The reagent used to extract the lignin from soft woods is presumed to act on this group after the initial hydrolytic action by some sort of condensation-polymerization reaction with alpha hydroxypropioveratrone or one of its derivatives and fructose or one of its derivatives (such as furfuryl alcohol). In lignin prepared from hard woods the propioveratrone group is partially replaced by an alpha hydroxy propiosyringone group.

Klason, in 1920, suggested that coniferyl aldehyde is the basic "building stone" of lignin, and Freudenberg believes that dihydroxyphenyl glycerol is the true group. The fact that protocatechuic acid
is obtained when lignin is fused with potassium hydroxide does not indicate definitely which group is present in the molecule, but it does point clearly to the aromatic structure of lignin. All this evidence proves that the "building stone" of lignin, be it attached to a derivative of fructose, a hemicellulose, or cellulose, has a basic group consisting of the $C_6-C_3$ structure.

Numerous structures for lignin have been proposed, none of which explain all the experimental results. A few of them might be mentioned. Fuchs proposes a complex formula which he thinks is "an ideal hypothetical substance to which all chemical experience in the investigation of spruce lignin may be traced."

Freudenberg believes that the two structures below may be present in spruce lignin in admixture, each fifth group being a piperonyl residue.
He also suggests for beech lignin this structural unit.

In both cases, he believes the lignin to be combined with the hemicelluloses of the woods. The simplest formula suggested by Freudenberg and co-workers is the unit,

which presumably is repeated ten or twelve times by ether linkages to make up the lignin molecule. Norman says that this formula would account for the formation of phenolic substances of the coniferyl and vanillin type, but it assumes that lignin is homogeneous, and lignin has been shown by physical methods to be heterogeneous.
Molecular weight determinations vary greatly, but the trend lately has been to accept a unit of between 800-900. Hibbert, Brauns, and co-workers insist on a weight of 840, and recent work by Stamm on osmotic pressure measurements bear them out. It is to be understood that this figure may be a multiple of the molecular weight and is not necessarily the absolute molecular weight.

Diametrically opposed to the belief in the fundamentally aromatic nature of the lignin molecule is the theory of Hilpert and his associates who have advanced the theory that lignin as such does not exist in wood, but that it is a product of the action of strong mineral acids on the very sensitive, partially methylated carbohydrates present in the wood. Evidence for his hypotheses is evidenced from the fact that part of the material isolated as lignin and containing methoxyl groups is soluble in water after mild hydrolysis, and lignin itself is believed definitely insoluble in water. Furthermore, according to the literature, it has always been considered that an important difference between lignin and the humic substances is that the humic material contains scarcely any methoxyl groups. Since the work of Ritter and Kurth, who showed that such methylated carbohydrate material is present in spruce wood, this concept can no longer be upheld. Now the only difference between lignin and humic material that is definitely proven is that humic
substances contain carboxyl groups. Muller and Stalder in their work on chlorination of plant tissues admit that native lignin formation of the plant by the removal of water from the simple sugars is a distinct possibility, but that further experimental data are necessary. When determining pentosans by the Tollens method one is never sure that all the furfural is separated by distillation with hydrochloric acid, for furfural itself is known to form insoluble products with acids. To correct the determination, pure xylose and arabinose have been distilled with HCl and tables of correction factors built up. But the complex carbohydrates chemically combined in plant tissue probably act differently than do simple sugars in the free state, and it is possible that the action of strong mineral acids upon complex carbohydrates produces a greater amount of furfural condensation products which are non-volatile. Therefore, low apparent pentosan values are found. Hilpert and Meybier analyzed the residues obtained from the pentosan determination of various woods and found that as the distillation with hydrochloric acid was prolonged, the amounts of the residues remained nearly unchanged. However, the hydrogen contents decreased and the carbon values increased, indicating that water was being lost. The methoxyl contents of these residues were much smaller than those of lignin, but then the methoxyl groups of lignin are sensitive to boiling HCl. This was shown
by boiling spruce lignin with HCl, whereupon the methoxyl content changed from 15 per cent. to 11 per cent. These workers believe that these data indicate that lignin is not present as such in plant tissue but is a product of a reaction whose speed of formation is directly proportional to the increase in temperature. This statement, then, explains why a greater lignin content is obtained at the relatively high temperature of a pentosan determination and a lesser lignin value at the usual low temperatures of the lignin isolation process. Hilpert says that the difference in values found may be as great as 30 to 40 per cent. These residues from pentosan determinations can be methylated to about the same methoxyl content as acid lignin—another reason for considering them related to lignin. Hilpert and Peters from their work on benzylated spruce wood are convinced that alkali lignin and acid lignin are entirely different substances and not more or less impure varieties of the same substance.

One of Freudenberg's best proofs that lignin has a fundamentally aromatic nature is the formation of Hg compounds by the action of mercuric acetate, whereby one HgOAc group replaces a hydrogen in the ring. Mercuric acetate itself is believed not to add on a double bond for subsequent analysis shows only one acetate group for each mercury atom in the product. On the other hand Hilpert doubts that any mercury
would enter the ring under the conditions employed. First, it must be made clear that mercury compounds which have added at a double bond can be hydrolyzed with dilute mineral acids. They also react instantly with ammonium sulfide to form HgS. If mercury atoms actually enter the ring, the product becomes quite inert to both ammonium sulfide and mineral acids. Among the known ring compounds tested was vanillin which took up mercury quickly and the resulting compound could not be cleaved on boiling with HCl. Spruce wood previously extracted with alcohol-benzene was treated with mercuric acetate in glacial acetic acid. It apparently added mercury at a double bond for the product acted immediately with ammonium sulfide and the mercury could be removed with hot dilute hydrochloric acid. Mercury was even taken up at room temperature by spruce wood, and it was found that treatment with cold dilute hydrochloric acid removed it again. Straw and spruce lignins took up 43 per cent mercury when treated in the same manner. In all cases, treatment with dilute hydrochloric acid removed nearly all of it. This behavior of lignin indicates that mercury acts at a double bond rather than adding at a ring, thereby refuting one of Freudenberg's strongest arguments of aromatic structure and making it improbably that lignin is composed of aromatic constituents. Hilpert and his colleagues therefore believe that any aromatic constituents obtained from lignin are formed by the
action of chemical reagents in the isolation process and are not preformed in wood.

In order to disprove Hilpert's claim that mercury adds at a double bond in lignin, Moore and Hibbert treated fully methylated methanol lignin with hydrogen in the presence of catalysts and low temperatures and pressures. These are optimum conditions for the reduction of open-chain ethylenic linkages, but entirely negative results were obtained, indicating no ethylenic linkages in the lignin building unit. That lignin is preformed and of an aromatic nature is most generally accepted now. Hibbert, et al., support the view that isolated lignin has both aromatic and non-aromatic properties and is a combination of both types of organic compounds.

If these workers do not believe that lignin is formed from the carbohydrate constituents in the plant a great number at least hold with the concept that lignin is chemically united with the polysaccharides.

Reactions of Lignin

"The appearance of lignin varies from a very light tan amorphous powder to an almost black friable resin, depending on the conditions of isolation, drying, age and origin." Braun's native lignin is a light cream, almost white powder. Using isolated butanol lignin as an example, (i.e. lignin prepared by treating wood with butyl alcohol and sodium hydroxide..."
in an autoclave followed by precipitation of the lignin with acid) the following solubilities are reported: "Insoluble to very sparingly soluble in water, dilute hydrochloric acid, dilute sodium bicarbonate, petroleum ether, mineral oil, chloroform, carbon bisulfide, trichloroethylene, acetone, ethyl ether, amyl alcohol, ethylene glycol, glycerol, ethyl acetate, naphthalene, cyclohexanol; sparingly soluble to moderately soluble in methyl alcohol, ethyl alcohol, butyl alcohol, tri-ethanolamine, butyl acetate, benzene, xylene, nitrobenzene, turpentine; moderately soluble to extremely soluble in dilute sodium hydroxide, cold concentrated sulfuric acid, dilute sodium carbonate, glacial acetic acid, ethyl cellosolve, phenol, benzyl alcohol, vanillin, salicylic acid, aniline, beta naphthol, dioxane, pyridene, furfural, camphor, borneol, and sulfur." These were determined by shaking the dried powder in the solvent at room temperature or stirring it into a melted solid. Lignin does not have a definite melting point, illustrating its heterogeneous nature. Decomposition takes place before the boiling point is reached.

Oxidation with strenuous oxidizing agents such as potassium permanganate, nitric acid, hydrogen peroxide, hypochlorites, etc., yield, curiously, no intermediate compounds, but either unchanged products or greatly degraded materials (the lower fatty acids and dibasic acids such as
oxalic acid and succinic acid.)

"Lignin forms soluble salts with the lithium, sodium, potassium, ammonium, and vanadium ions, and insoluble salts with aluminum, barium, calcium, cupric, ferrous, ferric, lead, magnesium, mercuric, uranium, and zinc ions." These salts are thought by Bailey to be phenates, by virtue of the phenolic hydroxyl group. As we have seen in the previous discussion, lignin can be methylated, acetylated, benzoylated and sulfonated. Nitric acid produces a nitrated product rapidly.

The proof of the carbonyl group rested partially on the formation of a hydrazone when lignin is treated with phenylhydrazine.

It has been shown that lignin condenses with aldehydes and ketones in the presence of strong acids to form humic-like products.

With phloroglucinol-hydrochloric acid solution, isolated lignin gives a bright purple color, and with phenol and hydrochloric acid a bluish green coloration appears. According to Muller and Stalder the best method of telling if a tissue is lignified is the instantaneous orange coloration obtained when the wood is treated with chlorine. Sugars and furfural also give this color but not immediately.
Lignin was chosen as the topic for the introduction of this paper because it was present in large quantities in catclaw wood and hindered the isolation and purification of the hemicelluloses to a great extent.
PRELIMINARY TREATMENT OF THE WOOD

Catclaw wood, Acacia greggii, was the material from which the hemicelluloses in this investigation were obtained. It was gathered January 1, 1939, cut away from sapwood and sawed while still green, for this is such a hard wood that sawing is quite difficult when the wood is dry. The next step was grinding the sawdust in a Wiley mill to a fine powder which would pass through a screen of 1 mm. mesh. Because the wood was highly lignified and highly pigmented as well as impregnated with the usual lipids and waxes known to occur in woods, repeated extractions with cold and hot acetone, cold and hot ethanol and hot water were necessary. Three thousand grains of this deep red-brown powder was divided among six six-liter flasks to facilitate handling. At least four extractions with cold acetone and then eight extractions with hot acetone under a reflux condenser were required before the initial black filtrates changed to a tea color. Acetone removes soluble sugars, alcohols, acids, proteins, fats, resins and waxes. The wood was still very dark, so treatment of the wood with ethanol, first in the cold and then under reflux followed. Again the filtrates were extremely dark, and a total of twelve extractions were necessary before the filtrates became straw colored. Lignin and ligneous substances along with tannins were removed by this treatment. Lignin is not appreciably soluble in acetone.
and only moderately soluble in ethanol; therefore we cannot assume that at this point all the lignin has been removed. Without doubt lignin is the chief impurity, for it appears to be present in large quantities in this wood and is apparently the most difficult to remove. The wood was still quite dark and six extractions with water on a boiling water bath failed to lighten the color very much. At this point the test for starch on the water extract with iodine in potassium iodide was found to be negative, as was the Fehling's test after hydrolysis. It is questionable whether the water extractions are of much value for the amount of impurities water removed was relatively small.

Extraction of the hemicelluloses was accomplished by treatment of the wood with four per cent. sodium hydroxide at room temperature. Hot concentrated alkali is avoided because it may effect a degradation of the hemicelluloses; a too dilute alkali would probably eliminate any drastic change in the molecule, but it would not remove all the desired material; therefore, a moderate concentration of sodium hydroxide at room temperature was employed. Norman states that prolonged treatment with cold four per cent. sodium hydroxide removes not only the polyuronide hemicelluloses and lignin, but also non-uronide carbohydrate or cellulosan from cellulose. He points out that the latter is a second type of hemicellulose and that in hard woods it is a xylan,
fact neglected by many workers. To support his statement that the four per cent. base is too drastic a reagent, he offers results showing that a two per cent. sodium carbonate extraction followed by a brief chlorination and then treatment with 0.5 per cent. sodium hydroxide extracts the greater part of the hemicelluloses and removes the minimum amount of non-uronide carbohydrates. However, time did not permit both types of extractions to be carried out, and, since the four per cent. sodium hydroxide treatment is almost standard and the results of this investigation had to be compared with other work done at this university, four per cent. alkali was used as the extractant.

The first three extractions were carried out with occasional shaking for forty-eight hours, the last for four weeks; in each case a very dark brown solution resulted. This long extraction was unavoidable, since the work of precipitating the previous extractions was more pressing. The sawdust, now somewhat lighter, was washed thoroughly with water and the washings added to the extraction liquid. Each extract was kept separate and subsequently treated by itself to facilitate handling; however, now it is believed that time, effort and material would have been conserved had the extracts been combined in a manner suggested later. The last extract, after acidification and after the addition of four to five volumes of eighty-five per cent. alcohol, showed
that only a small amount of hemicellulose was present, indicating that all the hemicelluloses that could be removed without resorting to chlorination had been taken out.

Now, to determine whether pectic materials were present, the wood was treated with twentieth normal hydrochloric acid. The hydrochloric acid acts in such a way as to liberate the insoluble pectic acid from its calcium salt. The solvent used to remove the pectic acid was five per cent. ammonium hydroxide. The dark ammoniacal filtrate obtained was acidified with hydrochloric acid to reprecipitate pectic acid, but the amount of the very impure, very dark material resulting after filtration, washing and drying was too small to merit further investigation, amounting approximately to 0.3 gram from 5,000 grams of wood. Therefore, we assumed pectic content of catesaw wood was negligible, if not absolutely zero.
The various fractions of the hemicelluloses have been classified by Angell and Norris on the basis of solubility in water. Hemicellulose A is the one which is insoluble in water and comes down when the sodium hydroxide extract is made acid, hemicellulose B, the one which precipitates when one-half volume of acetone is added, and hemicellulose C, the one which precipitates when one or more volumes of acetone are present. It has been found at the University of Arizona that one volume of ethanol roughly corresponds to one-half volume of acetone. Because alcohol is more economical and more pleasant with which to work, it was substituted in all cases. Hemicellulose B was not found in this wood, just the water insoluble A and the water soluble C. In finding the optimum pH for precipitating hemicellulose A, that is, the hydrogen ion concentration at which the original sodium hydroxide extract would precipitate out hemicellulose A quickly, leaving a perfectly clear supernatant liquid, great difficulty was encountered with the first and second extractions. The method used in finding this pH was to put five c.c. of the sodium hydroxide extract in each of twenty test tubes, then to add from a pipette counted drops of 2 N hydrochloric acid, varying the drops by one or two between test tubes. After they were shaken, four or five test tubes at first glance appeared
to be within the satisfactory pH range, but after centrifuging, only one or two gave a supernatent liquid free from cloudiness. This indicated that the pH range for satisfactory precipitation was quite limited. Finding that twenty-five drops constituted one c.c., the correct amount of acid was calculated for the large bulk of the first extraction (8700 c.c.) and added. Although a considerable amount of precipitate came down, the liquid above was murky after standing three or four days. Even centrifuging did not give a clean separation. The attempt to adjust the pH by adding either acid or base was continued repeatedly until the original volume of the sodium hydroxide extract was almost doubled. The original volume was 8700 c.c. and the volume after all this manipulation was almost 15000 c.c. Then water was added to dilute the solution even more, the whole made basic again, and the optimum pH for a satisfactory precipitation determined as before. When the calculated amount of acid was added to this greatly diluted extract, the hemicellulose precipitated completely within a minute, leaving a very clear supernatant liquid which centrifuged easily in ten minutes. The same trouble was experienced with the second extraction, but not with the third and fourth. Therefore, it is concluded: 1. that there is an optimum pH at which hemicellulose A may be precipitated; 2. that the solution must not be too concentrated with hemicellulose (the third and
fourth extractions contained relatively small amounts of material); 3. that since subsequent additions of one volume of ethanol or one-half volume of acetone produced no hemicellulose B, it is presumed that if all the A is precipitated sharply in the above manner, no B should appear; 4. that the hemicellulose is not stabilized by change because various salts were added to a little of the extract in test tubes and no noticeable change occurred. It is suggested that rather than to dilute the first and second extractions with water as was done in this case, it might be feasible to dilute the first extraction by mixing it with the fourth and to dilute the second by combination with the third, thus eliminating the necessity of handling great quantities of liquid and also of manipulating four separate extractions. If a small amount of hemicellulose is expected, all extractions could be combined. The optimum pH found in this case was between two and three as indicated by Alka-acid test paper, but this test, of course, is a rough approximation and not to be relied on. Another advantage of effecting a fast, complete separation is that the hemicellulose can be centrifuged immediately before the hydrolytic action of hydrochloric acid is able to do appreciable damage. The long standing in acid solution described above may well have cleaved some of the long hemicellulose molecules into shorter segments. The precipitated hemicellulose A was removed
from the acidified solution by centrifugation. It was then dried by placing it first in ninety-five per cent. alcohol, then in absolute alcohol, and finally upon a porous plate. There were 74.34 grams of the impure brown material.

As was stated above, no precipitation occurred when one volume of ethanol was added to the filtrate from hemi cellulose A, indicating that no hemicellulose B is present. Addition of a large excess of eighty-five per cent. alcohol brought down hemicellulose C. The amount of alcohol required should not be less than four volumes and careful tests should be made on the supernatant liquid to insure complete removal of all alcohol insoluble substances. Centrifuging, washing and drying with alcohol were carried out as before. There were 57.89 grams of this impure fraction. Upon combining the filtrates from hemicellulose C and rendering them slightly basic (pH 8 according to Alka-acid test paper) a large amount of black material separated out. At first it looked flocculent but on settling became granular. It centrifuged very quickly, and when dried was slightly sticky and quite black. It was easily soluble in water and completely insoluble in absolute alcohol. Estor reported a similar precipitate under the same conditions. Scott also found an analogous substance.
PURIFICATION AND FRACTIONATION OF THE HEMICELLULOSES

Since the main impurity in the hemicelluloses was obviously lignin, purification was accomplished by oxidation of the extraneous material with liquid bromine in a slightly acid solution. The brown impure hemicelluloses were dissolved in forty times their weight of four per cent. sodium hydroxide and filtered through two thicknesses of filter paper to remove insoluble matter. The clear filtrate was made slightly acid with 2 N hydrochloric acid (pH about 6) and a small excess of liquid bromine added. This supply had to be replenished from time to time. After standing from sixteen to twenty-four hours with occasional shaking, enough alcohol was added to destroy completely the excess bromine and precipitate out all the hemicellulose. Longer standing was not deemed advisable for fear of the hydrolytic action of hydrochloric and hydrobromic acids on the hemicelluloses. The precipitate was allowed to settle, the clear liquid was siphoned off, and the precipitate was centrifuged as soon as possible. Centrifuging should be done with care for a very lachrimatory substance is formed when alcohol is added to destroy the bromine. This process in some cases had to be repeated three or four times before the material became perfectly white. The hemicelluloses were then washed free from chloride with ninety-five per cent. alcohol, freed from water with absolute alcohol and finally dried on a
clay plate. Dissolving the impure hemicellulose in dilute sodium hydroxide did not remove lignin, as lignin is very soluble in this reagent. Subsequent precipitation of the hemicellulose with alcohol and acid brings down the greater part of lignin. Since we cannot effect a good separation of the hemicellulose from lignin on the basis of solubilities, we must depend on the destructive action that bromine has on lignin. It will be recalled that when an oxidizing agent acts on lignin, either a slight change occurs or a complete degradation to small molecules results. The fact that the hemicellulose became perfectly white does not prove that it was pure; however, it does indicate the removal of lignin, and, since no starch was found in the wood at any time, it can be assumed that the product is now reasonably free from impurities.

In the process of fractionating hemicellulose A to A₁ and A₂ and hemicellulose C to C₁, C₂, and C₃, there was no sharp separation in any case, so it appears that these fractions are purely arbitrary. Although there was no indication that this fractionation of the hemicelluloses led to the separation of definite chemical entities from mixtures of hemicelluloses, it furnished the opportunity to demonstrate that hemicellulose A and hemicellulose C were not in themselves chemical entities, but mixtures. Just how complex these mixtures are has not been determined.
Subsequent analysis showed that $C_3$ was composed of much smaller molecules than was $C_1$. This fact accounted for the greater solubility of the $C_3$ fraction. Furthermore, the fact that a definite melting point cannot be obtained may indicate a mixture.

This fractionation was carried out by dissolving the purified hemicellulose $A$ in fifty times its weight of two per cent. sodium hydroxide and determining the optimum $pH$ for precipitation. If hemicellulose $A$ were a single substance, it should come down completely at this $pH$ since it is the water insoluble fraction, and furthermore, no precipitation should occur on the addition of alcohol. This was not the case. The optimum $pH$ for the precipitation appeared to be reached when 240 c.c. of 2 N hydrochloric acid were added to each liter, yet even after standing over night, the supernatant liquid was still cloudy. This precipitated fraction was called $A_1$. Fraction $A_2$ is that material which precipitated when a large excess of alcohol was added. Because treatment of the filtrate from $A_1$ with one-half, one, one and a half, etc. volumes of alcohol produced no clear separation and because the amount of hemicellulose $A_2$ present amounted only to about 2 grams compared to nearly 14 grams of $A_1$, no further fractionation was attempted.
Hemicellulose C was dissolved in two per cent. sodium hydroxide as above and fractionated. Hemicellulose C₁ is that which precipitated in a slightly acid solution with one-half volume of alcohol, though a clean separation was not obtained; hemicellulose C₂ is the one which came down with one volume of alcohol and gave quite a clear filtrate. That fraction which formed upon the addition of an excess of ethanol, four or more volumes, is designated C₃. After being thoroughly dried all these fractions are perfectly white, very light, fine powders. The percentage of hemicellulose obtained after purification amounted to 2.27 per cent. of the wood.
TABLE I.

HEMICELLULOSES DERIVED FROM 3,000 GRAMS OF CATCLAW WOOD

<table>
<thead>
<tr>
<th>Hemicellulose</th>
<th>Extraction</th>
<th>State of Purification</th>
<th>Weights of hemicellulose*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hemicellulose A</td>
<td>first</td>
<td>before bromination</td>
<td>54.6 grams</td>
</tr>
<tr>
<td></td>
<td>second</td>
<td>after one bromination</td>
<td>18.6 grams</td>
</tr>
<tr>
<td></td>
<td>third</td>
<td>after two brominations</td>
<td>0.7 grams</td>
</tr>
<tr>
<td></td>
<td>fourth</td>
<td>after one bromination</td>
<td>0.44 grams</td>
</tr>
<tr>
<td>Hemicellulose C</td>
<td>first</td>
<td>before bromination</td>
<td>14.2 grams</td>
</tr>
<tr>
<td></td>
<td>second</td>
<td>before bromination</td>
<td>23.27 grams</td>
</tr>
<tr>
<td></td>
<td>third</td>
<td>after two brominations</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>fourth</td>
<td>after one bromination</td>
<td>0.5 grams</td>
</tr>
<tr>
<td>Hemicellulose X</td>
<td>all extractions</td>
<td>before bromination</td>
<td>71.2 grams</td>
</tr>
<tr>
<td>Hemicellulose A</td>
<td>all extractions</td>
<td>completely purified</td>
<td>33.53 grams</td>
</tr>
<tr>
<td>Fraction A₁</td>
<td>all extractions</td>
<td>completely purified</td>
<td>13.76 grams</td>
</tr>
<tr>
<td>Fraction A₂</td>
<td>all extractions</td>
<td>completely purified</td>
<td>1.96 grams</td>
</tr>
<tr>
<td>Hemicellulose C</td>
<td>all extractions</td>
<td>completely purified</td>
<td>26.13 grams</td>
</tr>
<tr>
<td>Fraction C₁</td>
<td>all extractions</td>
<td>completely purified</td>
<td>5.39 grams</td>
</tr>
<tr>
<td>Fraction C₂</td>
<td>all extractions</td>
<td>completely purified</td>
<td>4.67 grams</td>
</tr>
<tr>
<td>Fraction C₃</td>
<td>all extractions</td>
<td>completely purified</td>
<td>2.59 grams</td>
</tr>
<tr>
<td>Hemicellulose X</td>
<td>all extractions</td>
<td>completely purified</td>
<td>8.48 grams</td>
</tr>
</tbody>
</table>

* In some cases the hemicellulose was not removed from solution and weighed until after the first or second bromination; consequently the weight of the crude hemicellulose as originally extracted from the wood is not available in all cases.

# Moisture incompletely removed.
ANALYSES OF THE HEMICELLULOSES

The per cent. moisture was determined by drying the hemicelluloses in an electric oven at 100-105 degrees Centigrade for one week. The per cent. ash was found by igniting small samples and blasting to constant weight. Care must be exercised in all weighings and manipulations because the hemicelluloses are very light, fine powders. From these two determinations correction factors were found, and all subsequent calculations were figured on the ash and moisture free basis. The per cent. pentosan was found by controlled distillation of the hemicelluloses with twelve per cent. hydrochloric acid and subsequent precipitation of the furfural formed with phloroglucinol. The method of Lefevre and Tollens (82) was employed to determine the amount of carbon dioxide produced when samples were boiled with dilute HCl. From this value the per cent. uronic anhydride minus its methoxyl groups was calculated by multiplying the per cent. carbon dioxide by four. The equivalent weight of the hemicellulose was found also assuming that one uronic acid was present in the simplest recurring unit of the hemicellulose molecule. By multiplying the equivalent weight by the per cent. pentosan and dividing by the molecular weight of anhydroxylonc (132), the number of pentose units per uronic acid was determined. (83) The semi-micro modification of the Keisel method was
employed in determining the per cent. methoxyl present. Knowing the percent. methoxyl and the per cent. carbon dioxide, the number of methoxyl groups per uronic acid was calculated. The total percentage of constituents can be found by adding the percentages of uronic anhydride, pentosan, and methoxyl.
HYDROLYSIS

In order to determine the constituents of the hemicelluloses, all fractions except X were combined and hydrolyzed by treatment with two per cent. sulfuric acid on a boiling water bath. Fifty-four grams of hemicellulose were added to 1000 c.c. of the dilute acid, and the reaction carried out for sixteen hours. Longer hydrolysis was not considered advisable because of the possibility of the degradation of the uronic acid itself after the liberation of the sugar. The light brown solution was filtered to remove the insoluble, black body X which appeared, and then barium carbonate was added to the clear filtrate to bring the solution just to the neutral point. The precipitates of barium sulfate and barium carbonate were filtered out and washed with a little water and proved to have no organic matter among them. The light brown solution was decolorized with a little Darco which had been previously boiled for about ten minutes with distilled water to remove any soluble material. After the carbon was filtered out, the solution was evaporated under reduced pressure at a temperature of 50-60 degrees to such a consistency that when added dropwise to a fairly large amount of warm absolute alcohol, a floculent, non-sticky precipitate of the barium salt formed.

* To account for the apparent discrepancy between the amount of hemicellulose purified and the amount hydrolyzed, it should be explained that additional hemicelluloses were obtained from extraction of another 600 grams of wood.
This operation is carried out carefully in a large evaporating dish with vigorous stirring. If the whole mixture is poured back into a Florence flask and heated gently on a water bath for about thirty minutes, the particles of barium salt will adhere to the sides of the flask, while the sugar will remain in solution. Then all the solution is poured off, the barium salt dissolved in a little water, evaporated down and precipitated as before. If this is done several times, and all the solutions containing sugar combined, a fairly complete separation is effected. After the last precipitation the barium salt is filtered, washed with a little absolute alcohol, dried as completely as possible by suction and then on a porous plate. The final product was not white but a light tan color.

The solution containing the sugars was evaporated under reduced pressure at a temperature of 50-60 degrees until a rather viscous liquid formed and then set aside to crystallize. The crystals which formed were washed with a little alcohol, the filtrate and washings evaporated again, and crystallization allowed to take place. The first two crops of crystals came down while the syrup was still warm, the last two crops precipitated in the presence of an equal volume of glacial acetic acid. The fact that the crystals set to a solid mass is our best evidence that only one sugar resulted from hydrolysis. This sugar was shown to be xylose. After recrys-
tallization the melting point was 146 degrees and a mixed melting point with pure xylose also gave 146 degrees. The boat shaped crystals of calcium bromide-calcium xylonate (83) appeared when Bertrand’s test for xylose was applied. No glucose was present because no fermentation with yeast occurred after standing six hours in a warm place. The yeast was not poisoned by any barium salt in the sugar, for when a little glucose was added to the mixture of yeast and xylose, fermentation took place within an hour.

Hydrolysis of 5.4 grams of hemicellulose I resulted in the isolation of a sugar and the salt of a low molecular weight polyuronide or "resistant nucleus" corresponding to the salt obtained upon the hydrolysis of all polyuronides. The sugar was identified as xylose by Bertrand’s test. Glucose was proved absent by the fermentation test described above. A determination of the pentosan value showed that there are about six pentose molecules present for every uronic acid unit. Since the percentages of uronic anhydride, methoxyl, and pentosan totalled nearly seventy per cent., there remains thirty per cent. unaccounted for. Therefore it is concluded that this hemicellulose which precipitated originally in a basic solution is similar to those precipitated in the usual acid solution.

Methyl pentose was proved absent from the hydrolytic products obtained from the hydrolysis of all of the hemi-
celluloses obtained from catclaw wood by sensitive qualitative tests using rhamnose and xylose controls. The tests employed were the naphthoresorcinol test, the orcinol test; and Rosenthaler's test.
CONCLUSIONS ON THE HEMICELLULOSES

The hemicelluloses isolated in this investigation conform to the general picture of hemicelluloses obtained from other woods. The simplest recurring units all contain a monomethoxy uronic acid joined to different numbers of poly-anhydro-xylose units. Hemicellulose A₁, the fraction which precipitated when the basic solution of hemicellulose A was made acid, was found to be the largest molecule with nineteen xylose units attached to the uronic acid. Hemicellulose A₂, the fraction which precipitated when the filtrate from A₁ was treated with an excess of ethanol, contains fourteen xylose units.

In the water soluble group, hemicellulose C₁ and hemicellulose C₂ are very much alike for each contains eleven xylose units attached to the monomethoxy uronic acid. The specific rotation is the only value on which they are not in close agreement. Hemicellulose C₃ is somewhat shorter, containing about eight xylose molecules.

Even hemicellulose X, the fraction which precipitated when the alcoholic filtrates from the C fractions were made basic, follows the general scheme. It was composed of six xylose units joined to a monomethoxy uronic acid.
Comparison of the Results Obtained from Catclaw Wood Before and After Chlorination.

Table II shows the results obtained before and after the chlorination of catclaw wood. The water insoluble hemicellulose $A_1$ before chlorination and the hemicellulose $A$ after chlorination are entirely similar. The uronic acid in both cases has roughly one methoxyl group. The slightly higher carbon dioxide value and the lower pentosan content before chlorination indicates only a smaller molecule. The $A_1$ before chlorination showed nineteen pentose units per monomethoxy uronic acid and the $A$ after chlorination twenty-two pentose units. These shorter molecules may be the result of hydrolytic action, for in the isolation of $A_1$, unusual care was taken to find the exact pH for satisfactory precipitation, thus extending the time during which the solution was acid to nearly two weeks as compared with the two days that the solution was acid in the separation of $A$ after chlorination. Consequently, with $A_1$, there existed more opportunity for hydrolysis. However, there is no definite evidence that dilute acids do hydrolyze the hemicelluloses in the cold. It has been suggested that a study be made of the actual effect of acids and bases and even water on the so-called "free" hemicelluloses. On the other hand, it is entirely possible that these shorter molecules exist as such in the wood itself, and hence they would
be the more readily removed by the extractant. Since hemicellulose A₂ before chlorination was precipitated in the presence of alcohol, it will be considered with the water soluble hemicelluloses. It will be noted that the members of this entire group, both before and after chlorination were strikingly similar except for the methoxyl content and a small variation in molecular size. Hemicellulose B after chlorination contained one and a half methoxyl groups and hemicellulose C contained exactly two methoxyl groups per uronic acid. As Cosulich pointed out, hemicellulose B might well be a mixture of her hemicellulose A and hemicellulose C present in the proper proportions to give the observed methoxyl value. In all cases the water soluble hemicelluloses before chlorination contain a smaller number of pentose units. As stated previously, this condition may be due in part to hydrolytic action. However, it seems more feasible to believe, and there is no evidence to the contrary, that these smaller molecules are present in the wood as such. The higher specific rotation values obtained after chlorination are to be expected on this basis alone.

The type of hydrolytic products found before and after chlorination were identical, and therefore it was concluded that all the hemicelluloses of catalaw wood are of the same general nature except for the methoxyl content of the water soluble group and the number of anhydro-xylose units bound
to the uronic acid, i.e., in the molecular size of the various hemicellulose fractions.

Pectin was not found in the wood before chlorination nor in the wood after chlorination.
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<th></th>
<th>% CO₂</th>
<th>% methoxyl</th>
<th>% pentosan</th>
<th>% uronic anhydride</th>
<th>equivalent weight</th>
<th>pentose units per uronic acid</th>
<th>methoxyl groups per uronic acid</th>
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<th>specific rotation</th>
<th>% ash</th>
<th>% moisture</th>
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Comparison of Results Obtained in this Investigation and Previous Investigations on Various Woods

The water insoluble hemicellulose obtained in this investigation was found to be very similar in composition to the corresponding fractions isolated in black locust sapwood, black locust heartwood, lemon wood, white birch wood, mesquite wood, and cottonwood. With the exception of white birch wood, all contain approximately one methoxyl group per uronic acid. The number of pentose units per uronic acid varies from nine to twenty-two units; however, most of the woods give values around eighteen units. Since catolaw wood before chlorination gave nineteen units and after chlorination about twenty-two units, rather high correlation is observed. Since all these hemicelluloses are found to be mixtures rather than chemical entities, these values are in good agreement.

The analyses of the water soluble fractions in catolaw again exhibit agreement with those of other woods. They all contain roughly one methoxyl group per uronic acid, with the exception of catolaw after chlorination mentioned previously. The number of pentose units per uronic acid vary from six to fifteen units, the average value falling around eleven. In this investigation the range of pentose units was eight to fourteen.
It was found that the hydrolytic products in all cases are entirely similar. Always a methylated uronic acid and a single sugar, xylose, are found as "building stones" or constituents of the complex carbohydrate. Therefore, it is concluded that the hemicelluloses of catolaw wood fit in closely with the general picture of hemicelluloses from other woods.
SUMMARY

1. Without resorting to chlorination, the hemicelluloses of catclaw wood, Acacia greggii, were extracted by treatment with four per cent. sodium hydroxide at room temperature, after the lipid, resins, etc. had been removed by the appropriate solvents.

2. Analyses were carried out for the purpose of determining the constituent units present and their quantitative relationship.

3. Hydrolysis of the hemicelluloses produced a mono-methoxy uronic acid and a sugar. The sugar was definitely identified as xylose.

4. A comparison was made between the hemicelluloses obtained without chlorination in this investigation and those obtained by Gosulich after chlorination. It was concluded that all the hemicelluloses in catclaw wood were similar in general nature. Thus evidence accumulates toward proof that the hemicellulose removed after chlorination is not a different type of hemicellulose, but a small fraction of the total hemicellulose protected by the lignin of the wood and released through the destruction of that lignin by the chlorine treatment.

5. No pectin was isolated in the wood before chlorination.
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<th>Water insoluble hemicelluloses (A)</th>
<th>% CO₂</th>
<th>% methoxyl</th>
<th>% pentosan</th>
<th>% uronic anhydride</th>
<th>equivalent weight</th>
<th>pentose units per uronic acid</th>
<th>methoxyl per uronic acid</th>
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<td>81.94</td>
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