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_Erickson, Donald Lindsay__ for the M.S. in Chemistry__

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Abstract Approved: ____________________________

(Major Professor)

The relation of lignin to the waste sulfite liquor problem has stimulated a vast amount of research aimed at finding out the chemical nature and constitution of this substance. The problem of the disposition of sulfite pulping waste is of vital interest to plant operators because the unused material represents an economic loss of approximately one-half of the wood and creates stream pollution problem. Lignin, constituting about one-half of the waste, is the object of most wood research. The nature and constitution of lignin is also of interest to those seeking an answer to the question of plant synthesis.

The meaning of the term "lignin" is arbitrary. In general, it can be defined as the non-extractive, non-carbohydrate part of woody tissue. Lignin is named more specifically after the reagent or method used in its isolation. Native lignin is lignin as it occurs in wood.

Methods of isolating or determining lignin involve the use of two types of reagents: (1) those that dissolve the cellulose leaving the lignin as a residue, and (2) those that dissolve the lignin. Type (1) reagents are for the most part strong acids and type (2) reagents, organic solvents.

Lignin can be acylated, acylated halogenated, nitrated, sulfonated and methylated. It has been oxidized to saturated and unsaturated aliphatic acids, and aromatic acids. It can be reduced to hydrocarbon. Among the products of fusion with alkali are oxalic acid, catechol and vanillin. Dry distillation has yielded acetone, methanol, acetic acid, eugenol, phenol, hydroxy benzenes, and saturated and unsaturated hydrocarbons.
Various formulas have been postulated to take into account the reactions of lignin. Kürschner's formula represents a polymer of the glycoside coniferin. Klason proposed a formula made up of guaiacol propane nuclei in linear polymerization. Freudenberg originally held a view similar to Klason's but pictured a much larger molecule. Phillips has suggested guaiacol and a hydroxypropyl substituted guaiacol as the building units. Fuchs has presented a unique formula containing nine rings. Hibbert has recently suggested that the molecule is a condensation-polymer of α-hydroxypropiovanillone or of this compound and α-hydroxypropiosyringone.

Benzyl alcohol lignin has been prepared and subjected to solvent extraction. The fractions obtained and the original lignin have been analyzed for carbon, hydrogen and methoxyl content. Results so obtained indicate that the benzyl alcohol lignin is a mixture of substances and is a degradation product of native lignin. Solvent extraction did not serve to resolve the benzyl alcohol lignin into pure substances that could be identified.
SOLVENT FRACTIONATION OF LIGNIN PREPARED FROM WESTERN HEMLOCK BY EXTRACTION WITH BENZYL ALCOHOL

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DONALD LINDSEY ERICKSON

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June 1939
Approved:

[Signature]
Assistant Professor of Chemistry
In Charge of Major

[Signature]
Head of Department of Chemistry

[Signature]
Chairman of School Graduate Committee

[Signature]
Chairman of State College Graduate Council
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I. INTRODUCTION

As long as wood is used as a source of cellulose fibers for paper pulp and the various products in the chemical cellulose field, the nature of the other part of the wood will command the interest of those connected with this problem. In the pulping process approximately one-half of the dry wood used never leaves the plant as a salable product. In the Kraft process it is burned and has a certain calorific value, but in the sulfite process it is not only a total loss but gives rise to a stream pollution problem that threatens to invite legal restriction. Among the classes of compounds that are known to be in this unused half of the wood are the extractives (resins, fats, oils, etc.), hemicellulose, tannins, and sugars, which together constitute roughly one-fourth of the wood. The other fourth of the wood has not been identified and is known only as lignin.

Any industry that discards half of its raw material is naturally awake to any possibilities of finding commercial uses for this waste material, and many uses have been proposed and patented for the use of waste
sulfite liquor. These have been thus far of superficial nature or limited to certain fractions of the liquor, and by no means represent a satisfactory solution to the problem. As a road-binder it can be used with very little processing but is water soluble. It has met with little success as a source of fertilizer. Among the commercial, derived products may be included vanillin, yeast, alcohol, and plastics.

Because it constitutes the major part of the waste and because its composition is unknown, lignin has attracted most of the chemical investigation conducted on the problem of wood waste. Of course the interest in lignin is not entirely inspired by commercial motives, as its elucidation would throw much light on the mechanism of plant synthesis. As long as its structure is unknown, it will be a puzzle to challenge the imagination and intrigue the wit of the intellectually curious. It is not here asserted that the identification of lignin would result automatically in a solution of the waste sulfite liquor problem, but it would certainly be a helpful basis for experimentation. Hibbert (11) has presented a theory of plant synthesis based on what he believes to be the building units of lignin.

From the time that de Candolle in 1833 applied the
name lignin (9) to the fiber-encrusting material of wood it has had only an arbitrary meaning. In general it may be defined as the non-carbohydrate, non-extractive part of woody material. It occurs in plants ranging from herbs to trees. Wherever rigidity is needed lignification has taken place, for it is the function of lignin to bind the plant fiber.

The term lignin as defined above has been applied to the non-carbohydrate, non-extractive part of wood as a whole and to parts thereof. Its meaning is made more specific when used in conjunction with the reagent used in the isolation of the lignin referred to. Synonymous with names so applied are lignins named after the originator of the method employing the appropriate reagent. Native lignin is lignin as it occurs in the wood. Its meaning is somewhat vague owing to the possibility that lignin in wood is held in chemical combination by the carbohydrates. Opinion on this point is divided. If so held, it is only by a bond severable by hydrolysis which would make native lignin the lignin complex of ligno-cellulose with hydroxyls attached at those bonds where it previously joined the cellulose. It is doubtful that lignin has ever been isolated by chemical means without modification, and the products ordinarily obtained are considered to be derivatives of native
lignin. When it is remembered that the wood tissue is heterogeneous, it seems probable that there is a cellulose-lignin interface away from which there is on one side, lignin-free cellulose and on the other cellulose-free lignin. Harris, Sherrard and Mitchell(10) are among those who believe that lignin and cellulose may be combined. They found wood to be less susceptible to acetylation before being subjected to hydrolysis than after. Bailey (1) has isolated lignin physically by cutting out the middle lamella. He obtained material containing 71.4% lignin. As suggested by Gortner (9) the two views can be reconciled if some of the lignin is assumed to be combined and some not.

The reagents used in the isolation of lignin are of two types: (1) indirect, those that dissolve the non-lignin material; and, (2) direct, those that dissolve the lignin. To the first class belong the strong acids, 40% hydrochloric acid (Willstätter method), 72% sulfuric acid (Forest Products method), phosphoric acid (Urban method), and cuprammonium solution (Freudenberg method). There are many solvents for lignin. Those most commonly used in its isolation are alkali, methanol, phenol, glycol, cellosolve, other higher alcohols, formic acid, and acetic acid. All but alkali and formic and acetic acid require the use of a small
percentage of an acid (usually hydrochloric acid) as an activator. In general the indirect method gives higher yields, the direct method giving as low as 5% of the wood in the case of methanol lignin. The Forest Products method gives the maximum yield which is 100% of the lignin or about 25% of the wood, the latter figure varying with the species of wood used. The Forest Products method is generally used as an analytical procedure to determine lignin content and frequently used to prepare lignin for experimentation. Because of the inert nature of the reagents of the indirect method the lignin is less subject to combination with the reagent than it is when prepared by the direct method. However, it is subject to hydrolytic action and changes resulting from heat. Harris, Sherrard and Mitchell (10) compared lignins obtained by the Forest Products, Willstätter, cuprammonium, etc. methods with regard to yield, methoxyl and carbohydrate content and found that Forest Products lignin is free of carbohydrates, contains all the methoxyl not accounted for in the carbohydrates, and is produced quantitatively. Willstätter and cuprammonium lignin contained carbohydrates and were low in methoxyl. Cuprammonium solution dissolves some of the lignin, resulting in a low yield. On the basis of methylation studies they concluded that Forest
Products lignin is most like native lignin.

Lignin contains only carbon, hydrogen, and oxygen. The very reactive nature of lignin has afforded opportunity for identifying a number of functional groups in the lignin complex. One of these, the methoxyl group, can be determined quantitatively by a simple routine procedure. It varies from 9% in phenol lignin to 17% in glycol lignin. It also varies with the species of wood. The reactions that lignin can be made to undergo include acylation, aroylation, halogenation, nitration, sulfonation, and methylation. Oxidation has yielded the following acids: formic, acetic, oxalic, succinic, fumaric, malonic, adipic, benzoic, phthalic, isophthalic, mellitic, hemi-mellitic, tri-mellitic, and anisic. It can be reduced to hydrocarbons. Fusion with alkali has yielded oxalic and a number of fatty acids, catechol, protocatechuic acid, and vanillin. Dry distillation has yielded acetone, methyl alcohol, acetic acid, eugenol, phenol, hydroxybenzenes, and saturated and unsaturated hydrocarbons. These reactions predicate the presence of the benzene nucleus and carbonyl, hydroxyl, and methoxyl groups.

Any attempt to correlate all the information about lignin reported by various investigators is complicated
by the fact that one cannot interpret reactions and analytical data indiscriminate of the source of the lignin. Lignin prepared from different species of wood by identical treatment may vary, for instance, in methoxyl content. As stated before, wide variations are found in lignins prepared by different methods. Not only does lignin vary with the species and method of preparation, but many "extracted" lignins have been shown to be either heterogeneous or accompanied by a fraction that would not precipitate under the same conditions.

Various formulas have been assigned for native lignin to take into account the properties displayed by it. These presume a homogeneous substance.

Körshner (15) has postulated a formula representing a polymer of the glycoside coniferin.

\[
\begin{align*}
\text{C} & \quad \text{OCH}_3 \\
\text{C} & \quad \text{CH}_2\text{OH} \\
\text{C} & \quad \text{OCH}_3 \\
\text{C} & \quad \text{CH}_2\text{OH}
\end{align*}
\]
Klason (14) was the first to propose that lignin was built up of units containing the benzene rings with side chain as nuclei. He was of the opinion that lignin is essentially a polymer, or linear condensation product, of coniferyl aldehyde or alcohol or both.

Freudenberg's (5) early formula for "primary" lignin gives a much larger molecule, namely:

This formula makes it hard to account for guaiacol, catechol, acetovanillone, etc., obtained from lignin sulfonic acids by Hibbert (19). Freudenberg (6) later changed his views to regard lignin as being condensed from the polymer types III and IV.
Phillips (17) has suggested that the fundamental building units are guaiacol (V) and n-propylguaiacol (VI) with hydrogen atoms substituted by hydroxyl groups in the n-propyl side chain.

\[ \text{V} \]

\[ \text{VI} \]

Fuchs (8) has proposed the following formula (VII) which has been set up so that it contains all the necessary parts to explain all known properties and reaction of lignin. Fuchs, however, doubts very much the correctness of this formula.
Although all the constitutional formulas presented have some basis in experimental fact, they fail to agree completely with all the facts now known about lignin. Naturally, being different they could not all be true of the same material. More recent work, although showing a definite difference in lignins in different woods, has pointed toward a far greater structural similarity than exists between these formulas and has opened the possibility that all native lignin may be composed of a few relatively simple building units.

Brauns and Hibbert (2) have established an empirical formula for native lignin from spruce wood. Analysis of phenol condensation products from four types of lignin showed them to be derived from the same building unit. Analysis of methylation and acetylation products showed the presence of five hydroxyl and five methoxyl groups in the building unit. It has a molecular weight of 872 and is represented by VIII.

\[(\text{OH})_5 \text{C}_4\text{H}_2\text{O}_6 (\text{OC}_3\text{H}_8)_5\] 

**VIII.**
Further work in Hibbert's laboratory (4) has given support to the idea that native lignin may be relatively simple. He was able to isolate by ethanolysis of spruce wood a compound which upon methylation yielded α-ethoxypropioveratrone (IX).

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \quad \text{C} \quad \text{CH} \quad \text{CH}_3 \\
\text{OCH}_3 & \quad \text{O} \\
\end{align*}
\]

IX.

This compound was also synthesized. He also synthesized α-hydroxypropiovanillone (X), which compound he found would polymerize-condense readily under the influence of dilute acid at room temperature to give a product very similar to lignin. These facts suggest that lignin in the wood may be a condensation-polymer of X, or even X itself, in which case the high molecular weight of extracted lignin could be accounted for by the polymerizing effect of the extracting treatment.

Maple yielded two ethanolysis products (13). In addition to the one obtained from spruce he isolated and identified α-ethoxypropiosyringone (XI).

\[
\begin{align*}
\text{H}_3\text{C} & \quad \text{O} \quad \text{C} \quad \text{CH} \quad \text{CH}_3 \\
\text{OCH}_3 & \quad \text{O} \\
\end{align*}
\]

XI.
A mixture of X and XI in maple would account for its higher methoxyl content.

The compounds (IX and XI) which Hibbert identified are derived from only small fractions of the total lignin and in the usual precipitation procedure practiced in isolating extracted lignin this fraction is not precipitated but remains in solution in the precipitating medium, which usually has been discarded. Hibbert (12) previously had reported a similar sort of fractionation in the case of phenol lignin where he obtained a dioxane-ether soluble and a dioxane-ether insoluble fraction, the former being only a small percentage of the total.

Many instances of heterogeneity of isolated lignin products could be cited and many fractionation studies have been conducted. Besides fractional precipitation, solvent extraction has been employed as a fractionation procedure.

As a step toward gaining an insight into the nature of benzyl alcohol lignin the latter procedure was applied in this work to this material. By using a number of solvents capable of reacting with lignin as well as dissolving it, it was hoped to obtain data enabling comparison of this lignin with other lignins in regard to molecular weight of building unit and hydroxyl and
methoxyl content.

Recently Friedman and McCully (7) have developed a method for extracting lignin employing benzyl alcohol. Working with Western Hemlock and White Fir they obtained yields of around 20% with about 10.0% methoxyl. The lignin for this study was prepared essentially in accordance with their method.
II. EXPERIMENTAL

Preparation of Lignin

Western Hemlock sawdust from clear, barkless sections of wood was ground in a ball-mill and screened through a 100-mesh screen. The wood flour thus obtained was extracted 10 hours in a Soxhlet extractor with a mixture of 2 parts of benzene and 1 part of ethyl alcohol by volume, dried at 105°C., extracted 10 hours with water, and again dried at 105°C. Forty grams of the resin-free material were constantly stirred for 1 hour at 105°C. with 400 ml. of benzyl alcohol and 34 ml. concentrated hydrochloric acid. The reaction was carried out in a 1-liter round bottomed flask with a standard taper neck into which was inserted a short straight section of standard taper glass tubing. This served as a reflux air condenser and the mixture was stirred through it. The mixture was filtered hot on a Büchner funnel and washed with 50 ml. of hot benzyl alcohol. The filtrate was allowed to cool and was then poured slowly into 4 liters of well-stirred ether. The lignin settled immediately and the liquid was filtered through a fine cloth. The filtrate was only slightly turbid. The lignin was
washed with about 500 ml. of ether. To insure complete removal of benzyl alcohol the product was given a prolonged Soxhlet-type ether extraction. Approximately 8 grams of lignin was thus obtained and was designated Lot 9-R-3.

Lignin yields previously prepared in essentially the same way but from 10 gram samples of wood were combined and designated Lot 6-R-6. These were collected on alundum crucibles but owing to the slow rate of filtration were not washed with sufficient ether to remove the benzyl alcohol completely. When the ether evaporated off the residue was not powdery but somewhat gummy. After being in the oven over night at 105°C it could be ground to a powder which was then freed of benzyl alcohol by prolonged ether extraction. The yield obtained was 19% of the wood.

A second precipitate was obtained from the filtrate from the first precipitate by concentrating under vacuum after distilling off the ether, and again pouring the benzyl alcohol solution into ether. This precipitate was found to represent about 4% of the wood, making a total yield of 23%. Since only a small percentage was not precipitated by a single precipitation no further effort was made to recover this portion, and no study was made of it other than
to determine its methoxyl content, which was found to be much lower than that of the main lignin precipitate.

In a similar manner, lignin was prepared from Western Hemlock using phenol as the solvent instead of benzyl alcohol, mol for mol, and hydrochloric acid in the same concentration as before as the activator. The lignin was precipitated from the phenol solution by pouring it into ether.

A third lignin was made by the use of 70% sulfuric acid in the manner known as the Modified Forest Products Laboratory procedure (18). Eight grams of resin-free wood flour was added to 80 ml. of 70% sulfuric acid, previously cooled in a stoppered flask to 10°C. The contents of the flask were added to 3 liters of water, mixed well, and boiled 3 hours under reflux. The lignin was allowed to settle and the solution decanted through an alundum crucible. The residue was washed into the crucible with 1 liter of hot water, dried and weighed as lignin. Yield equalled 40%.

The cellulose residue from the benzyl alcohol extraction of wood was treated with sulfuric acid as described above, and a yield of 19.5% lignin was obtained.
Fractionation

Approximately 500 mg. samples of lignin (9-R-3) were weighed into tared alundum crucibles and extracted 16 hours on a Bailey-Walker extraction apparatus with the following solvents: butyraldehyde, carbon disulfide, acetone, chloroform, methyl alcohol, ethyl acetate, formic acid, dioxane, glacial acetic acid, ethylene glycol monomethyl ether, diisoamyl ether, phenol and ethylene glycol. The material remaining in the crucibles was washed with water, using suction, and then extracted 4 hours, with ether, on the Bailey-Walker extractor, dried and weighed. The solutions containing the soluble portions were poured into tared weighing bottles, evaporated to dryness at 100°C. and weighed.

Determination of Methoxyl Content

The method used for determining methoxyl content was that described by Clark (3). Approximately 10 mg. of the sample to be analyzed was weighed on an analytical balance on a tared piece of cigaret paper. The paper was folded and rolled into a compact ball, care being taken not to lose any of the weighed material. The sample, together with a bumping tile, was then
placed in the boiling flask of the apparatus, which had previously been charged with 2.5 ml. of phenol and 5 cc. of constant-boiling hydriodic acid (Sp. G. 1.70). The flask was connected to the rest of the apparatus which consists of a scrubber containing a 5% cadmium sulfate solution and receivers containing 10 ml. of a 10% solution of potassium acetate in glacial acetic acid to which six drops of bromine had been added. Carbon dioxide was passed through slowly and uniformly and the flask heated so that the vapor height was about half the height of the air condenser. After 25 minutes the heating was discontinued and the receivers were washed into a 250 ml. Erlenmeyer flask containing 5 ml. of 25% aqueous sodium acetate solution. The solution was diluted to 125 ml. and about 18 drops of 90% formic acid was added and agitated to decolorize the excess bromine. One gram of potassium iodide was then added, followed by a few ml. of 10% sulfuric acid. The iodide released was titrated with 0.1 M sodium thiosulfate. The reactions involved are as follows:
R-CH₂-OCH₃ + HI → CH₃I + R-CH₂-OH
CH₂I + Br₂ → IBr + CH₂Br
2Br₂ + IBr + 3H₂O → HIO₃ + 5 HBr
2HIO₃ + 10 KI + 5 H₂SO₄ → 5 K₂SO₄ + 6 I₂ + 6 H₂O
I₂ + 2 Na₂S₂O₃ → Na₂S₄O₆ + 2 NaI

From these equations it is seen that one equivalent of methoxyl (mol. wt. 31) is equivalent to 6 equivalents of thiosulfate. The percentage of methoxyl is given then by the formulas:

\[
\frac{31 \times \text{Ml. of Thio.} \times \text{Norm. of Thio.}}{6 \times \text{Wt. of Sample}} \times 100
\]

In practice it was found possible to run as many as five determinations with one charge of phenol and hydriodic acid without loss of accuracy. To avoid a high result on the first determination of a series it was found necessary to first heat the phenol and hydriodic acid alone with passage of Carbon dioxide for one-half hour to remove alkoxy impurities in the chemicals. As a check on the accuracy of the method control determinations were run on pure vanillin at the start and finish of a series until it was apparent that this practice was satisfactory. Data are shown in Tables I and III.
Combustion Analysis

For combustion analysis the apparatus used was with slight modification that described by Natelson and Brodie (16). The essential parts are, in the order in which the gas passes through them: (1) an oxygen reservoir, (2) a preheater, (3) a bubble counter, (4) a purifying tube, (5) a combustion tube, (6) absorption tubes, and (7) guard tube.

In the construction of the preheater and combustion tube pyrex glass tubing (10 mm. internal diameter) was used. The heating coils of both the preheater and combustion tube were made as an integral part of each unit. The glass tubing was first covered with a sleeve of iron gauze to prevent expansion of the tubing in use. A 3/16 in. insulating layer of asbestos was then placed over the iron gauze. No. 26 Nichrome wire was then wrapped around the asbestos. To obtain uniform heating it was necessary to wrap the Nichrome wire closer at the ends than in the middle of the heating section. The coils were finally covered with a section of pipe covering. A total of about 18 feet of wire was used and when the two heating coils and a rheostat were connected in series and 110 volts applied it was possible to obtain
temperatures in both units just under the softening point of the glass.

The preheater was filled with copper oxide and since only carbon and hydrogen were to be determined only copper oxide was used to fill the combustion tube. Cerium oxide impregnated on pumice was used as the catalyst. The oxygen reservoir was made from a 2 liter flask by sealing a stop-cock to each end and a manometer to one end. The manometer was calibrated to read the volume of oxygen delivered after being filled from a cylinder. The purifying tube was a straight tube containing anhydrite at the inlet end and ascarite at the discharge end.

The moisture absorption tube was made from straight 10 mm. soft glass tubing. The barrel was divided into two chambers, a short (about 1 cm.) gas chamber at the inlet end, and an anhydrite chamber (about 11 cm.). These were separated by a glass membrane with a small orifice (about 0.2 mm.). Short nipples were made from 3 mm. glass tubing by constricting them at 2 places to about 0.2 mm. and fire polishing one end and enlarging the other for sealing to the barrel. After the barrel had been filled with anhydrite the nipples were sealed on. The ascarite tube was made in the form of a U-tube (10 mm. internal
diameter) 11 cm. in height. After filling with a few cm. of anhydronite at the discharge end and the remainder with ascarite, nipples similar to those used on the anhydronite tube but longer, were sealed on and bent at right angles. The tubes were always aspirated with dry carbon dioxide free air before weighing. The guard tube was an ordinary drying tube filled with ascarite and anhydronite.

Combustions were run on 20 mg. samples weighed into porcelain boats. After being placed in the combustion tube the sample was slowly heated with a quiet slightly yellow flame until only a black carbon residue was left. The flame was then made larger but not hotter. Complete removal of the sample was usually accomplished in 25 minutes. Throughout the heating oxygen was allowed to flow at the rate of 10-11 ml. per minute, which rate was maintained after the heating to sweep out the tube until a total of 600 ml. had passed through after 55 minutes. A volume of 600 ml. of oxygen is more than the recommended amount but it was found necessary for this particular apparatus. Complete removal of moisture from the combustion tube at the temperature allowed by pyrex required overnight washing with oxygen. The only practical operating procedure was to maintain a
balance between the moisture entering the copper oxide from the sample and the moisture swept out by oxygen. It was found that below 500 ml. of oxygen the moisture absorbed is comparatively sensitive to variations in oxygen volume, while above 500 ml. of oxygen a comparatively large variation in oxygen volume results in a small variation in moisture absorbed. Six hundred ml. of oxygen was selected as a safe amount to use. Data are shown in Tables II and III.

**Saponification**

Possibly presence of an ester linkage in benzyl alcohol lignin was tested for by attempting to saponify it. A sample of the material weighing 1.7 g. was refluxed with 80 ml. of 25% aqueous sodium hydroxide solution for 10 hours. The reaction mixture was extracted with about 100 ml. of benzene 3 times. When the benzene was evaporated, no oily droplets were visible in the water remaining nor would the residual liquid when mildly oxidized with hydrogen peroxide give a coloration with fuchsin aldehyde, indicating the absence of benzyl alcohol. The saponification was repeated using saturated alcoholic potassium hydroxide. The alcohol was evaporated off on a steam bath and the residue mixed with water and extracted
with benzene as before. Again there was no indication of benzyl alcohol. A third saponification was run to determine the saponification equivalent. This time 500 mg. of lignin was refluxed with 50 ml. of 1.125 N alcoholic sodium hydroxide. In another flask another 50 ml. of the alcoholic sodium hydroxide was refluxed without lignin to serve as a control. After 2 hours 2 ml. of the liquid was titrated with standard acid using phenolphthalein as indicator. The corrected titration value was 21.9 ml. of 0.0985 N acid. The saponification equivalent was calculated as follows:

\[
\frac{500}{50 \times 1.125 - \frac{50}{2} \times 21.9} = 213
\]
III. DISCUSSION

In Table I are shown the results of methoxyl and yield determinations obtained in the preparation of the lignin. It is to be noted that there is considerable variation in methoxyl content of the benzyl alcohol lignin from lot to lot. Lot 13-A L-5 was prepared by C. R. McCully (7). Evidently the methoxyl content is sensitive to slight variations in time, temperature or hydrochloric acid concentration present as catalyst.

Combining the methoxyl found in the precipitated Hemlock lignin (1a), the second precipitate (1d), and the cellulose residue (1e), it is evident that only 64% of the lignin originally present in the wood has been accounted for.

A reasonable explanation for this, which also agrees well with the values found for the methoxyl content of the lignin (other extraction methods have given as high as 17%), is that the methoxyl ether linkage has undergone a considerable degradation during the extraction. This results in a degraded lignin preparation, low in methoxyl. This is evident also in the case of White Fir. Such splitting off of methoxyl has been observed by other investigators (10,21)
The very low value for phenol lignin can be ascribed to condensation of phenol with lignin to give a compound of much higher molecular weight (2).

After comparing lignin extracted from wood by various solvents, Hibbert (2) has concluded that the formula \((\text{OCH}_2)_5 \text{C}_4 \text{H}_3 \text{O}_5 \text{(OH)}_5\) probably represents native lignin. He states further that during the extraction process there is a marked tendency for combination of solvent with one of the hydroxyls which is apparently more active than the other four; that methoxyls may be split off by hydrolytic action; and that nuclear condensation with the solvent may take place.

The methoxyl content of native lignin based on Hibbert's formula is 17.3%. Lower methoxyl content in the extracted lignin may then result from any one of these three causes. Examination of the carbon content values obtained with benzyl alcohol lignin (Table II) leads to the conclusion that in this lignin no combination has taken place with the benzyl alcohol. This was further borne out in the saponification experiments previously described.

If we accept Hibbert's formula for native lignin, the splitting off of one methoxyl group and its replacement by hydroxyl will result in a product
containing 14.5% methoxyl; splitting off of two methoxyl groups, 11.0%; and the splitting off of three methoxyl groups, 7.5%. It would appear that the benzyl alcohol lignin obtained in these experiments is probably a mixture of break-down products of native lignin, containing four, three, and possibly two methoxyl groups per molecule.

With this view in mind it was thought possible that such a mixture might be separated by the differences in solubility into fractions at least one of which would contain a single type of molecule. Accordingly, the benzyl alcohol lignin was subjected to extended solvent extraction using thirteen different solvents.

Table III shows data obtained on the resolution of benzyl alcohol lignin into fractions by solvent action. In every case but one, chloroform, it can be seen that the methoxyl content of the insoluble fraction is greater than that of the soluble fraction. The partial solubility of the lignin in these solvents is proof of heterogeneity and the correlation between methoxyl content and solubility is significant of what the difference between the components of the lignin might be. It will be noted that the methoxyl content values of the residues
(insoluble fractions) fall into two fairly distinct groups. In group I the methoxyl content varies from 12.0% to 12.4% and averages 12.25%. While in group II it varies only from 14.1% to 14.3% and averages 14.22%. This rather sharp division suggests the presence in the original lignin of at least three different compounds, having methoxyl contents of 14.22%, 12.25% and a value below 12% to account for methoxyl in the original lignin. However, the weight values for the residues do not bear out the conception that the residue is one of two compounds, unless it is assumed that in the case of the 14.22% methoxyl lignin some of it had been dissolved and that long enough extraction would dissolve it all, and that in the case of the 12.25% methoxyl lignin some of it had been dissolved as well as all the 14.22% methoxyl lignin. In other words some solvents dissolve the low-methoxyl compound leaving the high-methoxyl compound while others behave just oppositely. This hardly seems possible.

In spite of the failure of the residue weight value to support the idea that the residues are identical to one of two compounds, the methoxyl values for the residues present a comparative uniformity when contrasted with the assortment of values found for the extracts
(soluble fractions). These variations are accounted for in part by reaction of lignin with solvent. It should be pointed out that the method used for determining "methoxyl content" is not limited to methoxyl groups but is affected by other alkoxy groups. Thus the solvent can affect the methoxyl analyses in two ways: by introducing alkoxy groups; and by increasing the molecular weight without introducing alkoxy groups.

Further evidence of similarity in the residues as compared with the extracts is seen in the carbon and hydrogen composition. The variation of % carbon in the residues is 4.6% and in the extracts, 6.6%. The variation of % hydrogen in the residues is 0.83% and in the extracts, 1.33%.

Although the data show the residues to be more uniform than the extracts, it is evident that no resolution of benzyl alcohol lignin into single compounds can be accomplished by simple solvent extraction. Further attempts to learn more about this substance by fractionation should employ some other technique.

Table IV shows the balance between the weight and methoxyl content of the original lignin samples.
and the combined weight and methoxyl content of the fractions. The methanol and formic acid combined weights were low owing to spattering during the evaporation. This can also account for the low combined methoxyl content of the formic acid fractions. The excess combined weights in the cases of butyraldehyde and acetic acid are undoubtedly the result of reaction between these solvents and lignin. The butyraldehyde residue was a light yellow color in contrast to the original pinkish brown of the lignin. Although in the cases of methanol and ethylene glycol monomethyl ether (cellosolve) the source of additional methoxyl groups is obvious, the almost universally high combined methoxyl content is hard to explain.
A discussion has been presented to point out why there is an interest in the nature of lignin and the meaning of the term "lignin". General methods of isolating and determining lignin have been described. The present status of our knowledge of the chemistry of lignin has been discussed.

Benzyl alcohol lignin has been prepared and subjected to solvent extraction. The fractions obtained and the original lignin have been analyzed for carbon, hydrogen and methoxyl content. Results so obtained indicate that benzyl alcohol lignin is a mixture of substances and is a degradation product of native lignin. Solvent extraction did not serve to resolve benzyl alcohol lignin into pure substances that could be identified.
TABLE I
MISCELLANEOUS METHOXYL AND YIELD DETERMINATIONS

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<th></th>
<th>Yield</th>
<th>% of wood</th>
<th>% Methoxyl</th>
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<tr>
<td>1. Benzyl Alcohol Lignin from Western Hemlock</td>
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</tr>
<tr>
<td>(a) Lot 9-R-3</td>
<td>20.0</td>
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</tr>
<tr>
<td>(b) Lot 6-R-6</td>
<td>19.0</td>
<td>13.3</td>
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</tr>
<tr>
<td>(c) Lot 13-A L-5</td>
<td>21.1</td>
<td>11.1</td>
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</tr>
<tr>
<td>(d) 2nd Precipitate (Lot 9-R-3)</td>
<td>4.0</td>
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<tr>
<td>(e) Cellulose Residue from Lot 9-R-3</td>
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<td>2. Benzyl Alcohol Lignin from White Fir</td>
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</tr>
<tr>
<td>(a) 1st Precipitate</td>
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<tr>
<td>(b) 2nd &quot;</td>
<td>1.5</td>
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<td>3. 70% H₂SO₄ Lignin from Western Hemlock</td>
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<tr>
<td>4. Phenol Lignin from Western Hemlock</td>
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<td></td>
<td>2.81</td>
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<td>5. Wood Flour</td>
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<td>(b) White Fir</td>
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The above methoxyl values are in all cases the averages from several determinations.
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<th>% C</th>
<th>% H</th>
<th>% O</th>
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<td>Hemlock Wood Flour</td>
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<td>6.38</td>
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<td>3.</td>
<td>70% H₂SO₄ Lignin from Hemlock</td>
<td>58.6</td>
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<td>4.</td>
<td>Phenol Lignin from Hemlock*</td>
<td>53.8</td>
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<td>5.</td>
<td>Benzyl Alcohol Lignin, 13-A L-5*</td>
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<td>Sucrose</td>
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<td>Vanillin</td>
<td>62.9</td>
<td>5.38</td>
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</table>

*Single determination; other values are averages of several determinations.
### TABLE III

**FRACTIONATION OF BENZYL ALCOHOL LIGNIN**

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<tr>
<th>Solvent</th>
<th>Grams of Lignin</th>
<th>Grams of Residue</th>
<th>Grams of Extract</th>
<th>% Methoxyl</th>
<th>% C</th>
<th>% H</th>
<th>% O</th>
<th>% Methoxyl</th>
<th>% C</th>
<th>% H</th>
<th>% O</th>
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<td>% Methoxyl x Wt. of Residue mg.</td>
<td>% Methoxyl x Wt. of Extract mg.</td>
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V. BIBLIOGRAPHY


