The Institute of Paper Chemistry

Appleton, Wisconsin

Doctor's Dissertation

An Investigation of Spruce Thiolignin

by C. Edward Ahlm

June, 1940

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AN INVESTIGATION OF SPRUCE THIOLIGNIN

A thesis submitted by

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June, 1940

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

EDITORIAL OFFICE

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INTRODUCTION

AND

HISTORICAL SURVEY

Thiolignin is the scientific term which has been selected for the lignin derivative isolated from wood by the action of a cooking liquor made up of the active chemicals employed in the kraft pulping process; namely, sodium sulfide, sodium hydrogen sulfide, and sodium hydroxide.

A survey of the lignin literature reveals that very little attention has been paid to the problem of determining the constitution and chemical properties of thiolignin or to the mechanism of the reaction taking place between lignin and the chemicals used in the kraft pulping process. Many investigators have determined the pulping properties of these chemicals in respect to the pulp produced, but only a few have made any effort to study their effect on the lignin dissolved in the black liquor.

The first investigation of thiolignin was carried out in 1911 by Klason and Segerfelt (1). They isolated thiolignin from a commercial sulfate black liquor by precipitating it with carbon dioxide and extracting the precipitated product with chloroform to remove any soluble impurities. According to their analysis thiolignin has the following composition: C, 63.3 per cent; H, 5.24 per cent;

and CH_3O, 12.0 to 12.8 per cent. No sulfur determination was mentioned.

In this precipitation method the hemicelluloses and pentosans which are soluble in the alkaline black liquor are precipitated with the lignin. Since these carbohydrates are insoluble in chloroform and no other effort was made to remove them, the lignin was undoubtedly contaminated with carbohydrate material. An indication of the validity of this assumption is the relatively low methoxyl content of the lignin.

Twelve years later Andersén and Holmberg (3) carried out an investigation on thiolignin which they isolated by adding hydrochloric acid to a black liquor obtained from a commercial sulfate cook of coniferous woods. They fractionated their thiolignin into an alcohol-soluble fraction called alpha-alkali lignin and an alcohol-insoluble fraction called lambda-alkali lignin. These lignin fractions were used as starting materials for hydrogen-peroxide oxidation experiments in which the lignin was completely degradated into water-soluble compounds, such as formic, acetic, oxalic, malonic, and succinic acids. The analyses which they gave for the two thiolignin fractions are tabulated below.

	Alpha-Alkali Lignin %	Lambda-Alkali Lignin %
CH_3O	10.7	12.3
C	63.4	66.5
H	5.1	5.8
S	2.5	1.95
Ash	5.6	1.65

Both fractions differ in their chemical composition which may be partially due to their high ash content. The authors do not mention whether the analytical values are calculated on an ash-free basis. If this is done, the data are changed to the following:

	Alpha-Alkali Lignin %	Lambda-Alkali Lignin %
CH_3O	11.3	12.5
C	67.2	67.6
H	5.4	5.9
S	2.6	1.98

Compared with other lignins the carbon content is rather high and the methoxyl content is low. This may indicate that the sulfate waste liquor came from a rather drastic cook. The low sulfur content, on the other hand, contradicts this statement. The dependence of the methoxyl and sulfur content upon the cooking conditions will be discussed later.

Hanson (4), in a study of the effect of sulfidity in the kraft pulping process, carried out several experimental cooks with sodium hydrogen sulfide as the cooking agent. In one series of cooks he isolated thiolignins with sulfur contents varying from 6.05 to 10.72 per cent and methoxyl contents varying from 13.36 to 11.67 per cent. In another series of similar cooks he obtained thiolignins with sulfur contents varying from 4.82 to 5.52 per cent.

In a laboratory experiment carried out in 1938 as a part of the lignin course at The Institute of Paper Chemistry (5)

Willstätter spruce lignin with a methoxyl content of 14.8 per cent was cooked with a 10 per cent solution of sodium sulfide for one hour at 170° C. During this operation the lignin went completely into solution and on precipitation gave an almost quantitative yield of a thiolignin with a sulfur content of 3.7 per cent and a methoxyl content of 14.4 per cent. As a result of this experiment it was pointed out that, when a molecular weight of 850 is assumed for the lignin building-unit, the sulfur content of 3.7 per cent is in very good agreement with the value of 3.6 per cent which is calculated for the entrance of one sulfur atom per lignin unit. The increase in the molecular weight of the lignin unit by the entrance of the sulfur atom also accounts for a decrease in the methoxyl content from 14.8 to 14.3 per cent.

PRESENTATION OF PROBLEM

A survey of the lignin literature reveals the fact that crude thiolignin has been isolated from kraft black liquors by acidification with mineral acids. The products so obtained are undoubtedly contaminated with colloidal sulfur and carbohydrates.

Preliminary experiments have shown that crude thiolignin can be purified easily by dissolving it in dioxane, centrifuging, and precipitating the clear solution in anhydrous ether. The product so obtained is in the form of a fine tan powder with physical characteristics very similar to those possessed by native lignin.

In a recent article Brauns (6) reported the isolation of native lignin from black spruce in the form of a fine powder without changing its chemical composition. He established the presence of four hydroxyl groups, four methoxyl groups, and a carbonyl group in his product by acetylation and methylation studies using diazomethane, dimethyl sulfate, and methanol as the methylating agents.

In view of the similarity of the physical characteristics of thiolignin and native lignin, a chemical investigation of thiolignin conducted along the lines employed by Brauns should enable one to determine the type of groups present in thiolignin.

EXPERIMENTAL SECTION

DESCRIPTION OF EXPERIMENTAL METHODS

In this investigation many experimental procedures are used repeatedly; therefore a preliminary discussion of these methods will avoid needless repetition.

The organic solvent selected for spruce thiolignin and its derivatives was 1,4-dioxane. Pure dioxane was prepared by refluxing the commercial solvent over metallic sodium for 16 hours and then distilling off the dioxane from the residues formed by the reaction of the sodium with the glycol, alcohols, and water present in the impure solvent. This purification process was repeated in order to be certain that the last traces of impurities were removed.

The purification process used for thiolignin and its derivatives consisted of precipitating the thiolignin from its dioxane solution with anhydrous ether. In most cases the purification process was repeated until a product was obtained which had the same methoxyl content after another purification. The lignin material to be purified is first dissolved in dioxane and then centrifuged and filtered through black ribbon filter paper (Carl Schleicher and Schull) to remove any insoluble material. Sufficient dioxane is used so that a 10 per cent solution of lignin is obtained. This concentration is optimum because a more dilute solution gives a precipitate too fine

to be centrifuged and a more concentrated solution gives a precipitate so coarse as possibly to occlude some dioxane and other impurities. Occluded dioxane will cause the precipitated lignin to become gummy on drying. The precipitation process consists of adding filtered dioxane solution in fine drops to a centrifuge jar containing anhydrous ether vigorously stirred with a mechanical stirrer. Only 4 cc. of dioxane can be precipitated satisfactorily in 100 cc. of ether, for a greater proportion of solvent would not permit the lignin to be quantitatively precipitated. After each addition of 4 cc. of dioxane, the precipitate is centrifuged and the supernatant ether-dioxane solution replaced with fresh ether. After the final increment of dioxane is added to the centrifuge jar, the dioxane is washed from the precipitated lignin by stirring the product twice with fresh ether and twice with petroleum ether. After standing overnight in the suspended condition, the precipitated lignin is centrifuged, the supernatant petroleum ether poured off, and the product dried in a vacuum desiccator over flake caustic and concentrated sulfuric acid.

Prior to analysis, all precipitated products were dried at least three hours in an Abderhalden oven held at 100° C. The drying pistle contained phosphorous pentoxide and was evacuated during the drying period to a pressure of 10 to 15 mm. of mercury.

Methoxyl determinations were carried out according to Institute Method 18, lignin determinations according to Institute Method 425, carbon, hydrogen, and ash determinations according to

Institute Method 706, and mercury determinations according to the electrometric method of Scott (7).

Sulfur determinations were made according to the following procedure. Between 100 and 160 mg. of sample are weighed out in a glass capsule and sealed in a Carius tube containing 2 cc. of fuming nitric acid. The tube is heated in a Carius furnace for four to six hours at a temperature of 230 to 250° C. After the tube has cooled, it is washed out with distilled water into a beaker containing 0.1 g. of sodium chloride. The resulting solution is evaporated to dryness on a waterbath and then treated with 5 cc. of 15 per cent hydrochloric acid. The acid solution is again evaporated to dryness and the residue taken up with 50 cc. of 10 per cent hydrochloric acid. Several cubic centimeters of a hot 10 per cent solution of barium chloride are added. After digesting several hours at 80° C., the precipitate is filtered, ignited, and weighed.

In this section the carbon and hydrogen determinations are reported on an ash-free basis; all other determinations are reported on an ash-containing basis.

PREPARATION OF THIOLIGNIN

The composition of any lignin isolated from wood by a pulping process depends not only on the type of chemicals used but also on the cooking variables, such as chemical ratio, liquor to wood ratio, heating schedule, maximum cooking temperature. Since it is

impossible in any one investigation to determine the effect of all of these variables on the composition of thiolignin, only the effect of the most important variables such as cooking time, chemical ratio, and chemicals were studied.

Preparation of Wood for Cooking Process

The wood used for the preparation of thiolignin was freshly cut sticks of black spruce. The sticks were reduced to sawdust and then extracted for 24 hours in a Soxhlet extractor with a solvent mixture composed of equal parts by volume of benzene and 95 per cent alcohol. The extracted sawdust was spread out on a screen and the solvents allowed to evaporate. After the sawdust had dried, it was extracted with distilled water and filtered on a Büchner funnel. The damp sawdust was again spread out on a screen and allowed to airdry. These extraction processes theoretically removed all the resins and sugars contained in the original wood. Moisture determinations were made on the airdried sawdust in order that yield calculations could be made on the ovendried basis.

Preparation of Cooking Liquors

Stock solutions of C.P. sodium hydrogen sulfide and of C.P. sodium sulfide were prepared by dissolving the hydroscopic salts in distilled water. Since the moisture contents of the crystalline salts were not known, it was necessary to titrate the stock solutions in order to find out their concentrations. The following procedure

was used in titrating these stock solutions.

Two cubic centimeters of stock solution are pipetted into a 250-cc. Erlenmeyer flask containing 7 cc. of standard sulfuric acid (1 N) and 50 cc. of distilled water. The contents of the flask are heated to boiling and held at that temperature until no hydrogen sulfide can be detected with lead acetate paper in the vapors issuing from the flask. The flask is allowed to cool and the excess sulfuric acid back titrated with standard sodium hydroxide (0.2 N), using phenolphthalein as the indicator.

The cooking liquor for each cook was made by diluting the correct stock solution with distilled water.

Cooking Conditions

The cooking conditions for the experimental cooks made in this investigation are listed in Table I.

Cooking Procedures

Cook 1

Airdried sawdust (309 g. or 282 g. ovendry) was placed in a stainless steel autoclave having a capacity of approximately five liters, and 2691 cc. of cooking liquor containing 119 g. of sodium hydrogen sulfide were added. The autoclave was closed and then partially immersed in a wax bath having an initial temperature of

TABLE I

GENERAL COOKING CONDITIONS

	Cook 1	Cook 2	Cook 3	Cook 4	Cook 5
Chemical Agent	NaSH	NaSH	Na_2S	Na_2S	NaSH
Concentration, Expressed as Equivalent NaOH, %	3	3	3	3	6
Chemical Ratio, Based on Wood and Equivalent NaOH, %	30	30	30	30	60
Time at Maximum Cooking Temperature, hr.	1.5	3.5	1.5	3.5	3.5

Note: The following variables were constant for all cooks.

1. Straight line temperature rise to maximum cooking temperature.
2. Time to maximum cooking temperature, 65 min.
3. Maximum cooking temperature, 160° C.
4. Time required to cool digester from maximum cooking temperature to 90° C., 1-1/2 hr.

150° C. The autoclave was heated on a straight line temperature-time curve; a period of 65 minutes was required to reach a maximum cooking temperature of 160° C. The temperature of the cook was determined by means of a thermometer inserted in a thermometer well which extended nearly to the center of the autoclave. The autoclave was held at the maximum cooking temperature for one and one-half hours and then lifted out of the wax bath and allowed to air-cool to a temperature of 90° C. Approximately one hour was required for the digester to cool.

The autoclave was opened and its contents filtered through a cotton cloth placed in a large Büchner funnel. The Büchner funnel was inserted in the neck of a 12-l. round-bottom flask to which a vacuum line was attached. Sufficient vacuum was applied to the flask so that the black liquor was drawn slowly into the flask. The black liquor adhering to the pulp was displaced with distilled water. Care was taken to add the wash water to the funnel at such a rate that no air was sucked through the pulp. Sufficient wash water was used so that the combined volume of the black liquor and washings was about 11 liters. The filtering and washing process was carried out as rapidly as possible in order to avoid oxidation of the thiolignin in the alkaline solution by air.

The filtrate was acidified with hydrochloric acid until acid to Congo red paper. During the acidification process large quantities of hydrogen sulfide gas were evolved as a direct result of the neutralization of the sodium hydrogen sulfide contained in the black liquor. As the black liquor approached neutrality, a copious

amount of a light yellow flocculent precipitate was thrown down. This slurry was allowed to settle overnight; then the supernatant liquor was decanted and filtered through filter paper placed on a Büchner funnel. The settled precipitate was then transferred to the funnel and washed. The thiolignin precipitate formed such a compact cake that two days were required to complete the washing process. The crude thiolignin was spread out on a porous plate and partially dried.

The washed wood meal was pressed, weighed, and carefully sampled for moisture determinations. The yield was 178.2 g. or 63.3 per cent of the ovendried weight of the original extracted sawdust. For analytical purposes a sample of the wood meal was washed a second time with distilled water in order to remove the last traces of black liquor. The wood meal was then acidified with 1 per cent acetic acid, washed with distilled water, airdried, and ground in a microhammer mill. The airdried product was analyzed for its lignin content, and sulfur and methoxyl determinations were carried out on the lignin residues obtained from the lignin determination:

Lignin content of digested wood meal	16.0%
Methoxyl content of lignin	15.2%
Sulfur content of lignin	1.6%

Purification of Thiolignin

Cook 1

The crude thiolignin contained free colloidal sulfur and some carbohydrate material. To remove these impurities, the crude thiolignin precipitate was dissolved in dioxane and centrifuged. The insoluble residue was suspended several times in fresh dioxane and then ignited with a flame. The characteristic blue flame of burning sulfur was observed, and it was concluded that this residue was primarily sulfur.

The clear dioxane solution was concentrated under reduced pressure to a volume of approximately 200 cc. During this operation fresh dioxane was periodically added to the concentrate in order that all the water present in the original dioxane solution would be carried over into the condensate. The removal of the last traces of water was extremely important because any moisture remaining in the dioxane solution would cause the thiolignin to become gummy when it was precipitated in ether. The concentrated dioxane solution was diluted with fresh dioxane to make approximately a 10 per cent solution and then precipitated into ether in the conventional manner. The precipitated lignin was washed twice with ether, twice with petroleum ether, and dried in a vacuum desiccator over flake caustic and concentrated sulfuric acid.

The dry dioxane purified thiolignin was treated for the second time with fresh dioxane. Part of the thiolignin product was

insoluble in dioxane and was centrifuged out. (This fraction will be discussed later.) The clear dioxane solution was precipitated and dried in the conventional manner.

Methoxyl	14.3%
Sulfur	3.1%

To make certain that the thiolignin had been purified to a constant methoxyl content, the twice-purified product was given a third purification from dioxane solution into ether. The purified product was analyzed:

Methoxyl	14.32%
Carbon	64.17%
Hydrogen	5.62%
Sulfur	3.18%
Ash	1.94%

A comparison of the methoxyl contents of the thiolignin after the second and third precipitation indicated that a product with a constant methoxyl content had been obtained.

The dioxane-insoluble material obtained from the second purification process was washed with fresh dioxane, anhydrous ether, and petroleum ether. After standing overnight under petroleum ether, the product was centrifuged, the supernatant liquor poured off, and the product dried in a vacuum desiccator over flake caustic and concentrated sulfuric acid. The analysis of this fraction was:

Methoxyl	10.3%
Sulfur	2.94%

The lower methoxyl and sulfur contents of the insoluble material indicate that this residue was contaminated with some carbohydrate material. To confirm this hypothesis, the dioxane-purified thiolignin and the insoluble residue were tested for carbohydrates with Fehling solution. The following procedure was used:

One-tenth of a gram of sample was treated with 2 cc. of 72 per cent sulfuric acid and allowed to stand at room temperature for two hours. The acid was diluted to a 3 per cent concentration and heated on a steambath for three hours. The solution was then neutralized with sodium carbonate, filtered, concentrated to a small volume, and tested with Fehling solution.

The insoluble material reduced Fehling solution, but the purified thiolignin had no effect. Hence, it was concluded that the purification process had removed all the carbohydrate material.

The ether-dioxane solution obtained in the first purification process had a light yellow color. In order to make certain that the thiolignin was not being separated into two fractions, the ether-dioxane solution was concentrated at atmospheric pressure to a viscous mass, dissolved in dioxane, and precipitated into ether in the conventional manner. The methoxyl content of this product was practically the same as the dioxane purified thiolignin.

Methoxyl	14.49%

Therefore, it may be concluded that this second fraction was due to the partial solubility of thiolignin in ether containing 2 per cent of dioxane.

In order to determine that the once purified thiolignin did not contain free sulfur, the thiolignin was extracted for eight hours with carbon disulfide in a Soxhlet extractor. The extracted material was dried in a vacuum desiccator and purified with dioxane in the conventional manner. A comparison of the analysis of the extracted and nonextracted thiolignins shows that no material is removed by the carbon disulfide extraction; therefore, the dioxane-purified thiolignin does not contain free sulfur.

Dioxane-purified thiolignin:

Methoxyl	14.32%
Sulfur	3.18%

Thiolignin extracted with CS_2 and purified with dioxane:

Methoxyl	14.38%
Sulfur	3.05%

When the carbon-disulfide-extracted thiolignin was dissolved in dioxane, an insoluble residue was obtained which was washed with dioxane, ether, and petroleum ether and dried in a vacuum desiccator over flake caustic and concentrated sulfuric acid.

Methoxyl	9.44%
Sulfur	2.03%

The low methoxyl and sulfur contents indicated that this product is contaminated with carbohydrate material.

Spruce thiolignin is a tan-colored powder soluble in dioxane, pyridine, alkali, and alcohol, slightly soluble in acetone, and insoluble in carbon bisulfide, chloroform, ether, and benzene.

Cooks 2, 3, 4, and 5 were made in the same way as Cook 1; therefore, only the experimental data of these cooks will be given.

Cook 2

Yield of pulp	58.7%
Lignin in pulp	12.7%
Methoxyl in lignin	15.1%
Sulfur in lignin	1.61%

Analysis of thiolignin after successive precipitations from dioxane into ether:

Number of Precipitations	Analysis	
2	Methoxyl	13.9 %
3	Methoxyl	14.12%
4	Methoxyl	14.06%
	Carbon	64.21%
	Hydrogen	5.58%
	Sulfur	3.03%
	Ash	1.35%

Cook 3

Yield of pulp	60 %
Lignin in pulp	15.6%
Methoxyl in lignin	15.1%
Sulfur in lignin	1.4%

Analysis of thiolignin after successive precipitations from dioxane into ether:

Number of Precipitations	Analysis	
2	Methoxyl	13.81%
3	Methoxyl	14.26%
4	Methoxyl	14.30%
	Carbon	63.81%
	Hydrogen	5.54%
	Sulfur	3.20%
	Ash	0.25%

Analysis of thiolignin extracted with carbon disulfide:

Methoxyl	14.30%
Sulfur	3.31%

Cook 4

Yield of pulp	54.8%
Lignin in pulp	10.0%
Methoxyl in lignin	14.4%
Sulfur in lignin	1.8%

Analysis of thiolignin after successive precipitations from dioxane into ether:

Number of Precipitations	Analysis	
2	Methoxyl	13.44%
3	Methoxyl	13.69%
	Carbon	63.53%
	Hydrogen	5.50%
	Sulfur	3.39%
	Ash	0.33%

Cook 5

Yield of pulp	47.7%
Lignin in pulp	3.17%
Methoxyl in lignin	12.88%
Sulfur in lignin	3.24%

Analysis of thiolignin after successive precipitations from dioxane into ether:

Number of Precipitations	Analysis	
2	Methoxyl	12.98%
3	Methoxyl	13.1 %
	Sulfur	3.97%

Analysis of thiolignin extracted with carbon disulfide:

Methoxyl	12.94%
Sulfur	4.22%

METHYLATION OF THIOLIGNIN WITH DIAZOMETHANE

The thiolignins isolated from the first four cooks were methylated in anhydrous dioxane solution with diazomethane. Under these conditions diazomethane will methylate weakly acidic or phenolic hydroxyl groups and carboxyl groups (8). Since the mercaptan group is more acidic than ordinary hydroxyl groups, it may be assumed that this group will be methylated with diazomethane.

The diazomethane methylations of the thiolignins isolated from the first four cooks were carried out in the same manner; therefore, only the details of the methylation of the thiolignin isolated from the first cook will be described.

Cook 1

Six grams of spruce thiolignin were dissolved in 50 cc. of dioxane and methylated with diazomethane prepared from 30 cc. of sodium glycolate and 15 cc. of ethyl N-nitroso-N-methylcarbamate. The diazomethane was prepared in a separate flask and carried into the dioxane solution by a slow current of nitrogen, the dioxane solution being kept at approximately 10° C. A strong nitrogen evolution, as well as a lightening of the dioxane solution, indicated that methylation was taking place. After all the diazomethane gas had been passed into the dioxane solution, the diazomethane-saturated solution was allowed to stand overnight and then centrifuged. Five cc. of the clear supernatant solution were precipitated in ether in the

conventional manner. The methylated product separated out as a light yellow flocculent precipitate.

Methoxyl	24.3%

The dioxane solution was remethylated with diazomethane prepared from 6 cc. of sodium glycolate and 3 cc. of ethyl N-nitroso-N-methylcarbamate. After standing overnight, a sample of the methylated thiolignin was precipitated and its analysis showed that it had the same methoxyl content as the sample taken after the first methylation. The constant methoxyl content indicated that the thiolignin was fully methylated with regard to diazomethane; therefore, the main portion of the dioxane solution was precipitated into ether in the conventional manner.

Methoxyl	24.28%
Carbon	65.44%
Hydrogen	6.06%
Sulfur	2.40%
Ash	1.82%

The thiolignins isolated from Cooks 2, 3, and 4 were methylated in the same manner.

Cook 2

Number of Methylations	Analysis	
1	Methoxyl	24.95%
2	Methoxyl	24.98%
	Carbon	65.29%
	Hydrogen	6.01%
	Sulfur	2.35%
	Ash	1.31%

Cook 3

Number of Methylations	Analysis	
1	Methoxyl	23.66%
2	Methoxyl	24.22%
3	Methoxyl	24.32%
	Carbon	64.94%
	Hydrogen	5.95%
	Sulfur	2.07%
	Ash	0.15%

Cook 4

Number of Methylations	Analysis	
1	Methoxyl	23.27%
2	Methoxyl	23.75%
3	Methoxyl	24.40%
4	Methoxyl	24.76%
	Carbon	65.82%
	Hydrogen	6.07%
	Sulfur	2.45%
	Ash	0.25%

All the diazomethane-methylated thiolignins were light tan powders soluble in dioxane, chloroform, acetone, pyridine, and a 1:1 mixture of alcohol and dioxane, slightly soluble in alcohol and benzene and insoluble in alkali, ether, and petroleum ether.

METHYLATION OF DIAZOMETHANE-METHYLATED THIOLIGNIN WITH METHANOL AND HYDROGEN CHLORIDE

Brauns (6) reports in his study of native lignin that diazomethane methylates an acidic hydroxyl group and a hydroxyl group formed by the enolization of a carbonyl group and that methanol and hydrochloric acid methylate a carbonyl group with the formation of an acetal. Since the two methylating agents behave differently, successive methylations with the two agents should indicate whether or not the carbonyl group is involved in the formation of thiolignin.

Seven-tenths of a gram of the diazomethane-methylated thiolignin of Cook 1 was dissolved in dioxane and treated with 65 cc. of absolute methanol containing 1 g. of hydrogen chloride. As soon as the lignin solution mixed with the methanol solution, the color of the dissolved lignin changed from a light brown to a dark brown. The mixture was refluxed three hours before the dioxane and methanol were removed under reduced pressure. The viscous residue was dissolved in dioxane, centrifuged to remove some insoluble material, and the clear solution precipitated in ether in the conventional manner. The methylation process changed the color of the dry diazomethane-methylated thiolignin from a light yellow to a dull gray.

Methoxyl 26.01%

Part of the methanol-methylated product was insoluble in dioxane. This residue was suspended successively in dioxane, ether, and petroleum ether before it was dried in a vacuum desiccator over flake caustic and concentrated sulfuric acid.

Methoxyl 24.99%

Methanol-methylated diazomethane-methylated thiolignin is a light gray powder soluble in dioxane but insoluble in ether and petroleum ether.

METHYLATION OF DIAZOMETHANE-METHYLATED THIOLIGNIN WITH SODIUM HYDROXIDE AND DIMETHYL SULFATE

Dimethyl sulfate is a more drastic methylating agent than diazomethane and will methylate aliphatic as well as acidic hydroxyl

groups; therefore, methylation of diazomethane-methylated thiolignin with dimethyl sulfate and sodium hydroxide should give a fully methylated product.

Two and one-half g. of diazomethane-methylated thiolignin of Cook 1 were treated with 30 cc. of acetone. The methylated thiolignin was not completely soluble in this solvent, and a few cubic centimeters of dioxane were added to dissolve the residue. Thirty-five cc. of 30 per cent caustic and 25 cc. of dimethyl sulfate were slowly added over a period of two hours to the thiolignin solution vigorously stirred with a mechanical stirrer. During the methylation process the temperature was not allowed to exceed 20° C. Acetone was periodically added to keep the methylated thiolignin in solution. After the methylating agents had been added, the reaction mixture was stirred for two hours and then allowed to stand overnight. The methylation procedure just described was repeated the next day and the solution again allowed to stand overnight.

The aqueous acetone solution was concentrated under reduced pressure at a temperature of 30° C. The methylated thiolignin was thrown out of solution as soon as the acetone was distilled off. The aqueous concentrate and insoluble residue were poured into a crushed ice and water mixture and filtered. The precipitate was ground in a mortar, refiltered to insure complete washing, and dried in a desiccator over flake caustic and concentrated sulfuric acid. A small sample of the methylated product was dissolved in dioxane and precipitated in ether in the conventional manner. The methylation procedure

was repeated until a product with a constant methoxyl content was obtained.

Number of Methylations	Analysis	
2	Methoxyl	31.35%
3	Methoxyl	32.44%
4	Methoxyl	33.64%
5	Methoxyl	33.64%
	Carbon	66.23%
	Hydrogen	6.35%
	Sulfur	1.29%
	Ash	1.18%

Dimethyl sulfate-diazomethane-methylated thiolignin is a light tan powder soluble in dioxane, acetone, pyridine, chloroform, and benzene but insoluble in alcohol, ether, and petroleum ether.

METHYLATION OF THIOLIGNIN WITH METHANOL AND HYDROGEN CHLORIDE

According to Brauns (6) methylation of lignin with methanol and hydrochloric acid methylates a carbonyl group with the formation of an acetal. Methylation of thiolignin with this agent should indicate whether or not the carbonyl group is involved in the reaction between lignin and sodium hydrogen sulfide.

Three and seven-tenths g. of thiolignin of Cook 1 were treated with a mixture of 15 cc. of dioxane and 20 cc. of absolute

methyl alcohol and centrifuged. The clear solution was poured into a flask containing 50 cc. of methyl alcohol and 4 g. of hydrogen chloride. As soon as the thiolignin solution became mixed with the alcoholic solution of hydrogen chloride, the color of the dissolved thiolignin changed from a light brown to a dull gray. The solution was refluxed for two and one-half hours and then allowed to stand at room temperature overnight.

The next day the methylated thiolignin solution was concentrated under reduced pressure to a viscous mass and treated with 100 cc. of a solution composed of equal parts of acetone and methanol. The solution was filtered and added drop by drop to 4 l. of distilled water vigorously stirred. The resulting colloidal suspension of methylated thiolignin was coagulated by the addition of a few grams of anhydrous sodium sulfate. The methanol thiolignin was filtered, washed well with distilled water, and dried in a vacuum desiccator over flake caustic and concentrated sulfuric acid. The product was dissolved in dioxane and precipitated in ether in the conventional manner.

Methoxyl	17.78%
Carbon	64.91%
Hydrogen	5.72%
Sulfur	3.26%
Ash	2.16%

Methanol thiolignin is a gray powder soluble in dioxane, 2 per cent caustic, pyridine, and acetone, slightly soluble in

chloroform, and insoluble in benzene, ether, and petroleum ether.

METHYLATION OF METHANOL SPRUCE THIOLIGNIN WITH DIAZOMETHANE

Seven-tenths of a gram of methanol-methylated thiolignin of Cook 1 was dissolved in 15 cc. of dioxane and methylated with diazomethane prepared from 10 cc. of sodium glycolate and 5 cc. of ethyl N-nitroso-N-methyl-carbamate. During the methylation process the dark color of the dioxane solution of methanol-methylated thiolignin changed to a light yellow. The dioxane solution was allowed to stand overnight before it was centrifuged and precipitated into ether in the conventional manner.

Methoxyl	25.91%

Diazomethane-methylated methanol thiolignin is a light tan powder soluble in dioxane but insoluble in ether and petroleum ether.

ACETYLATION OF THIOLIGNIN

One g. of thiolignin isolated from Cook 1 was dried in a vacuum desiccator over flake caustic and concentrated sulfuric acid and then dissolved in 12 cc. of pyridine. Eight cc. of acetic anhydride were added, and the reaction mixture was allowed to stand for two days at room temperature before it was poured into a cracked-ice and water mixture. The acetylated thiolignin, which was precipitated by the dilution process, was filtered and washed with distilled water. The product was dried in a vacuum desiccator over flake caustic and

concentrated sulfuric acid, dissolved in dioxane, and precipitated in ether in the conventional manner.

Methoxyl	11.62%
Carbon	62.55%
Hydrogen	5.50%
Sulfur	2.12%
Ash	0.00%

Acetylated thiolignin is a light tan powder soluble in dioxane, pyridine, benzene, chloroform, acetic anhydride, and acetone but insoluble in alcohol, ether, and petroleum ether.

ACETYLATION OF THIOLIGNIN METHYLATED WITH DIAZOMETHANE

One g. of diazomethane-methylated thiolignin of Cook 1 was acetylated in the same manner as described for the acetylation of thiolignin.

Methoxyl	21.50%
Carbon	64.16%
Hydrogen	5.80%
Sulfur	2.02%
Ash	0.12%

Acetylated diazomethane-methylated thiolignin is a light tan powder soluble in dioxane and pyridine but insoluble in ether and petroleum ether.

MERCURY DERIVATIVE OF SPRUCE THIOLIGNIN

One g. of thiolignin was dissolved in 60 cc. of glacial acetic acid and centrifuged. The clear solution was poured into a flask containing 50 cc. of glacial acetic acid and 50 cc. of a stock solution of mercury acetate prepared by dissolving 1 g. of mercuric oxide in 100 cc. of glacial acetic acid. As soon as the thiolignin solution was mixed with the mercury acetate solution, the insoluble mercury salt of thiolignin was precipitated. The reaction mixture was diluted with distilled water to a volume of 600 cc. and then centrifuged. A test of the supernatant solution with hydrogen sulfide indicated that an excess of mercury acetate had been used. The product was washed with distilled water, dried in a desiccator over flake caustic and concentrated sulfuric acid, dissolved in a mixture of dioxane and methanol, and precipitated in ether in the conventional manner.

Methoxyl	12.92%
Mercury	10.60%
Sulfur	3.34%

The mercury salt of thiolignin is a reddish-gray powder soluble in dioxane-methanol mixture, slightly soluble in acetone and insoluble in sodium hydroxide, ether, and petroleum ether.

PHLOROGLUCINOL TESTS

One-tenth g. samples of thiolignin derivatives were dissolved in a minimum amount of dioxane and then treated on a spot plate with a few drops of a 5 per cent solution of phloroglucinol dissolved in a 15 per cent solution of hydrochloric acid.

Thiolignin Derivative	Color Developed
Thiolignin	Dark grayish green
Thiolignin methylated with methanol and HCl	Greenish brown
Thiolignin acetylated with pyridine and acetic anhydride	No reaction
Thiolignin methylated with diazomethane	Yellow green
Thiolignin methylated with diazomethane and dimethyl sulfate	No reaction

TITRATION OF MERCAPTAN GROUP

One of the properties of the mercaptan group is its ability to be oxidized by iodine to the disulfide. This reaction is the basis of the iodometric titration of the mercaptan group in proteins developed by Kuhn, Birkofer, and Quackenbush (9). In their titration method the protein was dissolved in glacial acetic acid, treated with an excess of a standard solution of iodine in glacial acetic acid and, after standing, diluted with water and back titrated with standard thiosulfate solution. The difference between the iodine consumed by

the protein titration and a blank determination is a measure of the amount of iodine used in oxidizing the mercaptan group to the disulfide.

The following modification of the protein titration was used in an attempt to titrate the mercaptan groups assumed to be present in the thiolignin molecule.

One-half of a gram of thiolignin of Cook 1 was placed in a ground stoppered flask and treated with 50 cc. of glacial acetic acid freshly distilled over potassium permanganate. The thiolignin did not dissolve immediately; hence a few drops of water were added to the flask, which was then gently heated. After an hour the thiolignin was completely dissolved. Fifty cc. of a standard solution of iodine in glacial acetic acid (0.02 N) were added. The flask was immediately stoppered, shaken vigorously, and allowed to stand five minutes. One-hundred cc. of distilled water were then added and the excess iodine back titrated with standard thiosulfate solution (0.05 N). The end point was determined externally with starch-iodide paper or electrometrically by using the Cameron potentiometer. The amount of sulfur present in the thiolignin is calculated from the difference between the iodine consumed by the thiolignin and a blank. The values found in this way for the sulfur content of thiolignin were: 3.2, 2.9, 2.6, and 2.7 per cent. The sulfur content found by the Carius method was 3.2 per cent.

DISCUSSION OF EXPERIMENTAL RESULTS

CHEMICAL COMPOSITION OF SPRUCE THIOLIGNIN

The first part of this investigation is concerned with the problem of determining the degree to which the composition of spruce thiolignin is dependent on the conditions under which it is isolated. To solve this problem five experimental cooks were made using the same laboratory technique but different cooking conditions. The cooking conditions employed in carrying out each cook are given in Table I.

TABLE I

GENERAL COOKING CONDITIONS

	Cook 1	Cook 2	Cook 3	Cook 4	Cook 5
Chemical Agent	NaSH	NaSH	Na_2S	Na_2S	NaSH
Concentration, Expressed as Equivalent NaOH, %	3	3	3	3	6
Chemical Ratio, Based on Wood and Equivalent NaOH, %	30	30	30	30	60
Time at Maximum Cooking Temperature, hr.	1.5	3.5	1.5	3.5	3.5

Note: The following variables were constant for all cooks.

1. Straight line temperature rise to maximum cooking temperature.
2. Time to maximum cooking temperature, 65 min.
3. Maximum cooking temperature, 160° C.
4. Time required to cool digester from maximum cooking temperature to 90° C., 1.5 hr.

An idea as to the severity of each cook may be obtained by inspecting Table II.

TABLE II

ANALYSIS OF PULP

	Cook 1	Cook 2	Cook 3	Cook 4	Cook 5
Yield of Pulp, %	63.3	58.7	60.0	54.8	47.7
Lignin Content of Pulp, %	16.0	12.7	14.6	10.0	3.2
Methoxyl Content of Lignin in Pulp, %	15.2	15.1	15.1	14.4	12.9
Sulfur Content of Lignin in Pulp, %	1.6	1.6	1.4	1.8	3.2

Note: The methoxyl and sulfur determinations were carried out on the lignin residues obtained from the lignin determinations.

A comparison of the pulp yields obtained in Cook 1 with those in Cook 3, and of Cook 2 with Cook 4, shows that, for the same titratable alkalinity, the pulping action of sodium sulfide is slightly more effective than that of sodium hydrogen sulfide. The same conclusions can be drawn from a comparison of the lignin contents of the pulps.

The effect of increasing the length of time at which the cook is held at maximum cooking temperature on the pulping action of sodium hydrogen sulfide is shown by Cooks 1 and 2 and for sodium sulfide by Cooks 3 and 4. Lengthening the time increases to a slight degree the pulping action of each chemical.

The effect of chemical ratio and concentration of the cooking liquor on the pulping action of sodium hydrogen sulfide is shown by Cooks 2 and 5. These cooks were carried out under the same cooking conditions, except that in Cook 5 the concentration and chemical ratio were twice as great as in Cook 2. The yield of pulp as a result of increasing the concentration and chemical ratio in Cook 5 decreased from 58.7 to 47.7 per cent; the lignin content of the pulp decreased from 12.7 to 3.2 per cent.

A comparison of the methoxyl and sulfur contents of the various lignins left in the pulps shows that, as the cooks become more drastic, the methoxyl content decreases and the sulfur content increases.

The effect of the cooking variables studied on the composition of the thiolignin dissolved in the black liquor is shown in Table III.

TABLE III

ANALYSIS OF THIOLIGNINS

	Cook 1	Cook 2	Cook 3	Cook 4	Cook 5
Methoxyl Content, %	14.6	14.2	14.3	13.7	13.1
Carbon Content, %	64.2	64.2	63.8	63.5	----
Hydrogen Content, %	5.6	5.6	5.5	5.5	----
Sulfur Content, %	3.2	3.1	3.2	3.4	4.0
Ash Content, %	1.9	1.3	0.2	0.3	----

Note: All values are reported on an ash-free basis, except the methoxyl and sulfur contents of Cook 5 which are reported on an ash-containing basis.

From the above table it may be concluded that as the cooking conditions become more drastic, the methoxyl content of thiolignin decreases and the sulfur content increases. The difference in sulfur contents cannot account for the difference in methoxyl contents; therefore, it appears that, as the cooking conditions become more drastic, some methoxyl groups are split off.

In order to determine whether or not the thiolignins obtained from the various cooks had the same number of acidic hydroxyl groups, the thiolignins isolated from the first four cooks were methylated with diazomethane. The analysis of the methylated derivatives is given in Table IV.

TABLE IV

ANALYSIS OF THIOLIGNINS METHYLATED WITH DIAZOMETHANE

	Cook 1	Cook 2	Cook 3	Cook 4
Methoxyl Content, %	24.8	25.2	24.8	24.8
Carbon Content, %	65.44	65.29	64.94	65.82
Hydrogen Content, %	6.06	6.01	5.95	6.07
Sulfur Content, %	2.44	2.48	2.12	2.46
Ash Content, %	1.82	1.31	2.07	0.25

Note: All values are reported on an ash-free basis.

A study of Table IV shows that the methoxyl content of all the thiolignins increases to practically the same value. This indicates that the number of acidic hydroxyl groups is the same no matter

whether the thiolignin is isolated with sodium hydrogen sulfide or with sodium sulfide. It also shows that the methoxyl groups which are split off by the more drastic cooking conditions can be replaced. The carbon and hydrogen content of the products check remarkably well considering the amorphous nature of the material; the sulfur content, however, is much lower than can be accounted for by the increase in molecular weight due to methylation. The sulfur content of 3.2 per cent should have decreased to 3.0 per cent instead of 2.5 per cent as a result of the increase in methoxyl content of 10.7 per cent. It is not certain whether this decrease in sulfur content is due to the splitting off of sulfur during the methylation process or to the removal of a small fraction of thiolignin containing a high percentage of sulfur during the purification of the methylated product.

CHEMICAL STRUCTURE OF SPRUCE THIOLIGNIN

The second part of this investigation is concerned with a study of the chemical structure of spruce thiolignin. In carrying out this study a number of derivatives were prepared, the structural interpretation of which is based primarily on the work of Brauns (6) in his study of native lignin.

The first problem involved in the study of the structure of spruce thiolignin was to determine the molecular weight of its smallest building unit. The solution of this problem can be accomplished by three independent calculations which are based respectively on the analysis of thiolignin itself and its acetylated and mercury derivatives.

Spruce thiolignin has a methoxyl content of 14.6 per cent. If we assume that none of the four methoxyl groups found in the native lignin building unit are split off under the alkaline cooking conditions, then the molecular weight of the building unit of thiolignin is determined by Equation 1:

$$\frac{4 \times 31.02 \times 100}{X} = 14.6, \qquad (1)$$

in which X represents the molecular weight of the thiolignin building unit. The solution of this equation shows the molecular weight of thiolignin to be 849.

When spruce thiolignin is acetylated in pyridine solution with acetic anhydride, the methoxyl content is decreased by the addition of acetyl groups from 14.6 to 11.6 per cent. The molecular weight of the thiolignin building unit can be easily calculated from this datum if we first calculate the molecular weight of the acetylated building unit and then determine the number of acetyl groups introduced by the acetylation process. The molecular weight of the acetylated product is calculated by Equation 2:

$$\frac{4 \times 31.02 \times 100}{X} = 11.6, \qquad (2)$$

in which X represents the molecular weight of the acetylated building unit. The solution of this equation shows the molecular weight of the acetylated thiolignin to be 1069.

The number of acetyl groups introduced by the acetylation process can be calculated from the methoxyl content of the acetylated

product. If Y represents the number of acetyl groups, the solution of Equation 3,

$$\frac{4 \times 31.02 \times 100}{849 + Y(43.02 - 1)} = 11.6, \qquad (3)$$

shows that 5.1 acetyl groups have been introduced. (The same number of acetyl groups is obtained when the difference between the molecular weights of acetylated thiolignin and thiolignin is divided by the molecular weight of the acetyl group.)

The molecular weight of the thiolignin building unit is found from the molecular weight of the acetylated thiolignin building unit by subtracting the molecular weight of five acetyl groups and adding the molecular weight of five hydrogen atoms. When this is done, the molecular weight of the thiolignin building unit is found to be 859.

The molecular weight of the thiolignin building unit can also be calculated from the analysis of the mercury derivative if we first calculate the molecular weight of the mercury thiolignin building unit and then the number of atoms of mercury combined with each unit. The purified mercury derivative had a methoxyl content of 12.9 per cent, a mercury content of 10.6 per cent, and a sulfur content of 3.34 per cent.

The molecular weight of the mercury thiolignin building unit is calculated by Equation 4:

$$\frac{4 \times 31.02 \times 100}{X} = 12.9, \qquad (4)$$

in which X represents the molecular weight of the mercury thiolignin building unit. The solution of this equation shows the molecular weight of the mercury thiolignin building unit to be 962.

The number of mercury atoms reacting with each thiolignin building unit is calculated from Equation 5:

$$\frac{4 \times 31.02 \times 100}{854 + X200} = 12.9, \qquad (5)$$

in which X represents the number of atoms of mercury reacting with each thiolignin building unit. The solution of this equation shows that 0.52 atom of mercury is required. In other words, one atom of mercury reacts with two thiolignin building units to form the mercury derivative.

The molecular weight of the thiolignin building unit is found by subtracting 100, one-half of the atomic weight of mercury, from the molecular weight of the mercury thiolignin building unit. If this is done, the molecular weight of the thiolignin building unit is 862.

The average of the three values, 849, 859, and 862, found for the molecular weight of the thiolignin building unit is 857. The difference between the molecular weight of 857 for the thiolignin building unit and the molecular weight of 840 for the native lignin building unit is 17. Since this value is practically equal to the difference in atomic weight of sulfur and oxygen, the indication is that, in the reaction between sodium hydrogen sulfide and lignin,

one sulfur atom may replace one oxygen atom.

On the basis of the entrance of one sulfur atom into the thiolignin building unit, the theoretical sulfur content of thiolignin should be 3.74 per cent; the value found was only 3.2 per cent. The discrepancy between these two values can be explained by the possibility that some alkali lignin was formed along with the thiolignin.

The explanation of the previously mentioned discrepancy between the theoretical and actual sulfur contents of thiolignin is based primarily on the analysis of the mercury derivative. If one sulfur atom is present in the thiolignin building unit, then the theoretical sulfur content of the mercury derivative should be 3.35 per cent, which is the same as the observed value of 3.34 per cent. The theoretical sulfur content of the thiolignin building unit can be calculated from the sulfur content of the mercury derivative by multiplying its sulfur content by the ratio of the molecular weights of the two building units.

$$3.34 \times \frac{960}{857} = 3.74 \qquad (6)$$

This value for the theoretical sulfur content of thiolignin is the same as the value previously calculated. This sulfur analysis is also in agreement with the value reported for the thiolignin prepared by the action of sodium sulfide on Willstätter spruce lignin (5).

The formation of a mercury salt of thiolignin gives us not only an idea of the manner in which the sulfur is combined with the lignin, but also a means of separating alkali lignin from thiolignin. The fact that a mercury salt was formed indicates that the sulfur in thiolignin is attached in the form of the mercaptan group. The separation of alkali lignin from thiolignin depends on the fact that mercury acetate precipitates thiolignin from its acetic acid solution but does not react with alkali lignin.

An idea as to the nature and number of hydroxyl groups in thiolignin may be obtained by acetylation and methylation studies using diazomethane, dimethyl sulfate, and methanol as the methylating agents. Diazomethane in anhydrous dioxane solution, according to Brauns and Hibbert (8), will methylate the weakly acid or phenolic hydroxyl groups and carboxyl groups, whereas dimethyl sulfate will methylate all the hydroxyl groups except the carboxyl groups. It is quite probable that these methylating agents will also methylate the mercaptan group. The exact manner in which methanol reacts with thiolignin is not known. In native lignin it is believed that the carbonyl group assumed to be present is methylated with the formation of an acetal group.

When spruce thiolignin is acetylated with acetic anhydride the methoxyl content is decreased from 14.6 to 11.6 per cent. This decrease, as previously shown, corresponds to the entrance of five acetyl groups into the thiolignin building unit. This is the same

number of groups which are introduced into native lignin by the same treatment (6).

The theoretical sulfur content of the acetylated thiolignin is calculated to be 2.6 per cent, whereas the value of 2.1 per cent was actually found. This discrepancy may be caused by the presence of some alkali lignin in the thiolignin.

When spruce thiolignin is methylated with diazomethane in anhydrous dioxane solution, the methoxyl content increases from 14.6 to 24.8 per cent and the sulfur content decreases from 3.2 to 2.4 per cent. The number of methoxyl groups introduced by the methylation is calculated by Equation 7,

$$\frac{(4 + X)\ 31.02 \times 100}{857 + 14X} = 24.8, \qquad (7)$$

where X is the number of methoxyl groups introduced. The solution of this equation shows that 3.2 groups have been introduced. In the methylation of native lignin only two methoxyl groups were introduced (6).

The sulfur content of the methylated thiolignin should have decreased as a result of the increase in molecular weight from 3.2 to 3.0 per cent instead of to 2.4 per cent. It is not certain whether this discrepancy between the theoretical and actual sulfur contents is due to a splitting off of sulfur during the methylation process or to a loss of a fraction of thiolignin containing a high percentage of sulfur during the purification of the methylated product.

On methylation of diazomethane-methylated thiolignin with dimethyl sulfate and sodium hydroxide, the methoxyl content increases from 24.8 to 34 per cent, and the sulfur content decreases from 2.4 to 1.3 per cent. The number of methoxyl groups introduced by the successive methylation with diazomethane and dimethyl sulfate is calculated by Equation 8:

$$\frac{(4 + X)\ 31.02 \times 100}{857 + 14X} = 34, \qquad (8)$$

where X is the number of methoxyl groups introduced. The solution of this equation shows that 6.35 methoxyl groups were introduced. When native lignin was methylated with these agents only five methoxyl groups were introduced (6).

The sulfur content should have decreased as a result of the increase in molecular weight from 2.4 to 2.3 per cent. The discrepancy between this value and the theoretical value may be due to an alkaline hydrolysis of the methylated mercaptan group. A sulfur content of 1.3 per cent corresponds to 0.35 of a mercaptan group. If this group is methylated, then it is possible to account for the fractional number of methoxyl groups introduced by the dimethyl sulfate methylation.

When diazomethane-methylated thiolignin is acetylated with acetic anhydride the methoxyl content, as a result of the increase in molecular weight, is decreased from 24.8 to 21.5 per cent. The number of acetyl groups introduced is calculated by Equation 9:

$$\frac{(4 + 3.2)\ 31.02 \times 100}{857 + 3.2 \times 14 + X(43.02 - 1)} = 21.5, \qquad (9)$$

where X is the number of acetyl groups introduced. The solution of this equation shows the value of X to be 3.1. This is approximately the number of acetyl groups which are introduced into native lignin by this agent.

Methylation of spruce thiolignin with methanol and hydrogen chloride increases the methoxyl content from 14.6 to 18.2 per cent. The number of methoxyl groups introduced is calculated by Equation 10:

$$\frac{(4 + X)\ 31.02 \times 100}{857 + 14X} = 18.2, \qquad (10)$$

where X is the number of methoxyl groups introduced. The solution of this equation shows that only 1.1 methoxyl groups are introduced. In native lignin under the same conditions two methoxyl groups are introduced which are believed to be held by the formation of an acetal (6).

When methanol-methylated spruce thiolignin is methylated with diazomethane, or diazomethane-methylated spruce thiolignin with methanol and hydrogen chloride, products with the same methoxyl content (26 per cent) are obtained. The total number of methoxyl groups introduced by the two successive methylations is calculated by Equation 11:

$$\frac{(4 + X)\ 31.02 \times 100}{857 + 14X} = 26, \qquad (11)$$

where X is the number of methoxyl groups introduced. The solution of this equation shows that 3.6 groups are introduced.

An empirical formula for the spruce thiolignin building unit can be developed from a study of the analysis of thiolignin and its derivatives and a comparison of the calculations made in this investigation with those made by Brauns (6) in his study of native lignin. In developing this formula for the building unit of thiolignin, it is assumed that the empirical formula proposed by Brauns for native lignin is correct and that thiolignin is formed by the reaction of sodium hydrogen sulfide with native lignin.

According to Brauns, the native lignin building unit has a molecular weight of 840 and contains four methoxyl groups, four hydroxyl groups (one of which is acidic or phenolic), and an easily enolized carbonyl group. This carbonyl group gives rise to the enol and keto forms of native lignin.

Mercaptans form salts with the heavy metals (10); the formation of a mercury derivative of thiolignin, therefore, establishes the presence of the mercaptan group in thiolignin. A calculation made on the basis of the analysis of this mercury derivative (Equation 5) has shown that only one mercaptan group is introduced into each fundamental building unit having a molecular weight of 840.

In order to establish the location of this mercaptan group the following possibilities will be considered:

1. The sodium hydrogen sulfide reacts with one of the aliphatic or acidic hydroxyl groups, the net result of which is the substitution of a mercaptan group for a hydroxyl group.

2. The sodium hydrogen sulfide reacts with the lignin by the opening of an oxygen ring with the formation of a mercaptan group and a hydroxyl group. This hypothesis is suggested in a report on a lignin experiment carried out at The Institute of Paper Chemistry (5).

3. The sodium hydrogen sulfide reacts with the carbonyl group.

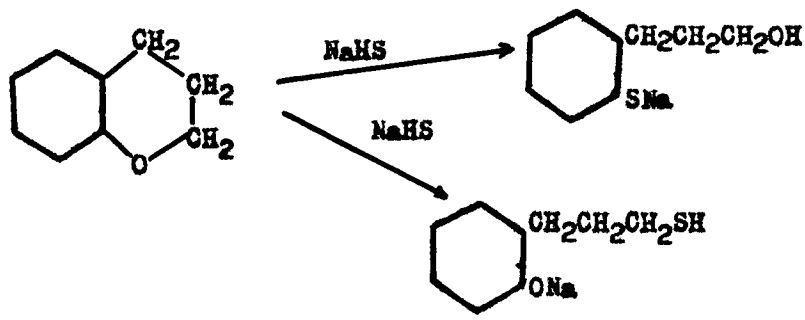
In native lignin, diazomethane methylates two hydroxyl groups, one of which is acidic or phenolic in character, whereas the other is assumed to be formed as a result of the enolization of the carbonyl group. Methylation of thiolignin with diazomethane introduces three methoxyl groups.

If in the formation of thiolignin the mercaptan group has replaced an acidic hydroxyl group, one or two methoxyl groups would be introduced, the number depending on whether or not the mercaptan group is methylated with diazomethane. Since three methoxyl groups were introduced, this possibility may be rejected. If, on the other hand, the mercaptan group had replaced an aliphatic hydroxyl group and had been methylated with diazomethane, three methoxyl groups would be introduced, a hypothesis which is in agreement with the experimental data.

When diazomethane-methylated native lignin is acetylated, three acetyl groups are introduced, a fact which indicates the presence of three aliphatic hydroxyl groups in the building unit of native lignin. If the mercaptan group had replaced one of these hydroxyl

groups and had been methylated with diazomethane, only two acetyl groups should be introduced. Experimentally it was found that three groups were introduced when diazomethane-methylated thiolignin is acetylated; therefore, the mercaptan group has not replaced any of the aliphatic hydroxyl groups.

If thiolignin is formed by the opening of an oxygen ring, a new mercaptan group and a new hydroxyl group should be formed. These new groups would be either phenolic or aliphatic in character, depending upon the manner in which the ring is opened.



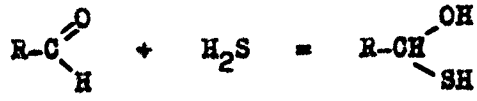
If thiolignin is formed by this reaction, the thiolignin building unit should contain five hydroxyl groups, four methoxyl groups, an easily enolized carbonyl group, and a mercaptan group. Experimentally it was found that five acetyl groups are introduced; therefore, this reaction can be rejected because acetic anhydride will acetylate the easily enolized carbonyl group.

When native lignin is methylated with methanol and hydrochloric acid, two methoxyl groups are introduced which are believed

to have formed an acetal. Methylation of thiolignin on the other hand introduces only one methoxyl group. This difference in behavior indicates that the carbonyl group is involved in the formation of thiolignin.

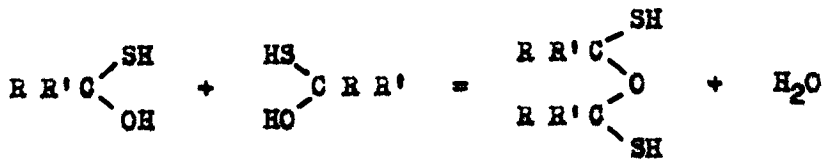
The manner in which sodium hydrogen sulfide reacts with the carbonyl group in lignin is unknown; however, it is believed that the reagent has been added to the carbonyl group in such a way that a hydroxyl group and a mercaptan group are attached to the same carbon atom.

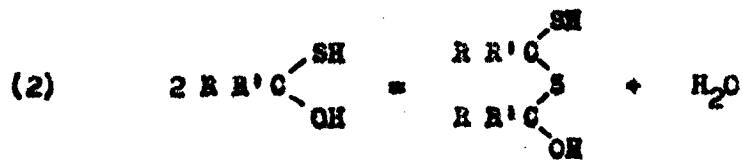
Unfortunately very little is known about the reaction of hydrogen sulfide or its alkali salts on aldehydes and ketones. In 1890 Baumann (11) studied the action of hydrogen sulfide on aldehydes and came to the conclusion that hydrogen sulfide reacts with the aldehyde group in the following manner:



These low molecular addition compounds condense with each other and with aldehydes; this condensation may take place in one of the following ways:

(1)



(2) 

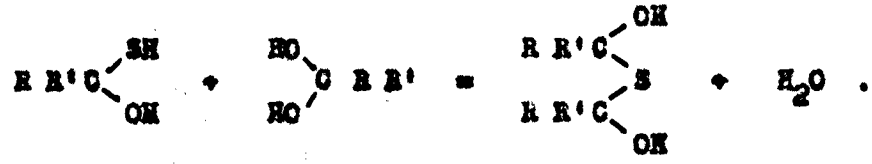
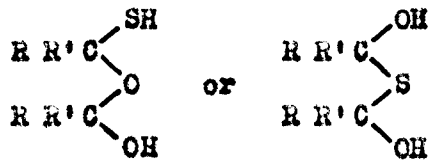
(3) 

TABLE V

COMPARISON OF THIOLIGNIN WITH NATIVE LIGNIN

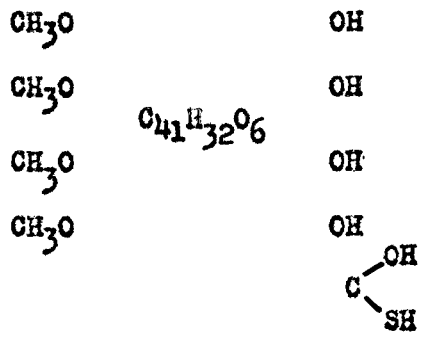
Lignin Derivative	Thiolignin			Native Lignin		
	No. of CH_3O Groups	No. of Acetyl Groups	CH_3O %	No. of CH_3O Groups	No. of OH or Acetyl Groups	CH_3O %
1. Thiolignin or Native Lignin	4	——	14.6	4	4 OH	14.8
2. No. 1 acetylated with acetic anhydride	4	5 Ac	11.6	4	5 Ac	11.8
3. No. 1 methylated with CH_2N_2	7	——	24.8	6	3 OH	21.4
4. No. 3 methylated with $(CH_3)_2SO_4$ + NaOH	10.3	——	34.0	9	——	31.3
5. No. 3 acetylated with acetic anhydride	7	3 Ac	21.5	6	3 Ac	18.9
6. No. 1 methylated with CH_3OH and HCl	5	——	18.2	6	4 OH	20.9
7. No. 3 methylated with CH_3OH and HCl	7.6	——	26.0	7	3 OH	24.4
	(After remethylation with CH_2N_2)					25.4
8. No. 6 methylated with CH_2N_2	7.6	——	25.9	7	3 OH	25.36

It is also possible that, in alkaline medium, hydrogen sulfide instead of water may be split off and the following typical condensation products formed:



This type of condensation might account for the loss of sulfur which occurred in the preparation of several of the thiolignin derivatives. Baumann stated that in the reaction between hydrogen sulfide and aldehydes in aqueous solution, in contrast to the case when dehydrating agents are present, no condensation takes place, but that the products of the reaction are always more or less complicated compounds which contain mercaptan groups and show the properties of mercaptans.

On the basis of Brauns's study of native lignin, Baumann's work with hydrogen sulfide and aldehydes, and the experimental results of this thesis (<u>see</u> Table V), the following empirical formula for thiolignin is proposed:



SUMMARY AND CONCLUSIONS

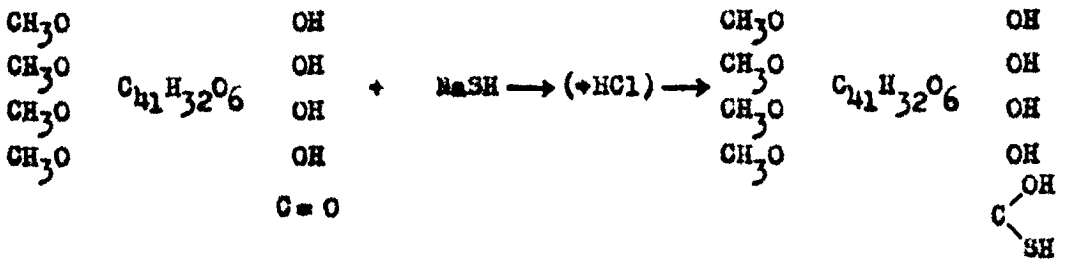
Thiolignin was prepared from black spruce with sodium hydrogen sulfide and sodium sulfide. The methoxyl content of the isolated thiolignins varied, depending on the severity of the cooking conditions, from 14.6 to 13.1 per cent; the sulfur content varied from 3.1 to 4.0 per cent.

The presence of the mercaptan group in thiolignin was established by the formation of the mercury derivative. The mercury and sulfur contents of this compound corresponded to the presence of one mercaptan group per lignin building unit.

Methylation of thiolignin with methanol and hydrochloric acid introduced one methoxyl group per building unit; methylation of native lignin with this agent introduced two methoxyl groups, which are believed to form an acetal with the carbonyl group. The difference in behavior of the two lignins indicates that in the formation of thiolignin the carbonyl group is modified by the sodium hydrogen sulfide to form a new group in which a hydroxyl group and a mercaptan group are attached to the same carbon atom. This appears to be one of the essential reactions occurring between lignin and the cooking liquor of a kraft cook.

In agreement with the preceding statements, thiolignin is believed to be formed in the kraft cook by the reaction of sodium

hydrogen sulfide with native lignin according to the following scheme:



Native Lignin

Thiolignin

The sodium salt of the product on the right is the main lignin product found in the black liquor of the kraft cook.

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