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Sulfite Cooking Process. II.¹ The Reaction between Thioglycolic Acid and Spruce Lignin

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In a recent paper, Holmberg² compared the reaction between thioglycolic acid and lignin with that between sulfurous acid and lignin and concluded that the mechanisms of the two reactions are identical. As a result of his intensive studies, he believed that a hydroxyl group of the lignin molecule reacts with the mercapto group of the thioglycolic acid through the elimination of water.

Hägglund and Carlson,³ on the other hand, claimed to have found that, in the sulfonation reaction of lignin in the sulfite cooking process, a new hydroxyl group is formed with the entrance of each sulfonic acid group into the lignin molecule. This newly formed hydroxyl group was found by Freudenberg⁴ to be phenolic in character.

In our work on the actual reaction taking place between lignin and sulfurous acid in the sulfite cooking process, it seemed desirable to study these conflicting theories and determine which is correct. Since lignin can be extracted by thioglycolic acid under relatively mild conditions and in a very good yield, and in a condition conveniently handled, the reaction of thioglycolic acid with native lignin in black spruce was studied with special regard to the nature of the hydroxyl groups.

Analytical data are given in Table I.

Experimental Part

Thioglycolic Acid Lignin from Black Spruce.—The following method is a modification of that proposed by Holmberg.⁵ Black spruce wood meal (270 g.) of 100 mesh, previously extracted with benzene-alcohol and hot water, was heated with a mixture of 150 g. of thioglycolic acid and 1500 cc. of 2 *N* hydrochloric acid for seven hours on a water-bath. The product was filtered, washed with water until neutral toward congo paper, air-dried, and extracted twice by suspending it in 2 liters of alcohol for forty-eight hours. The material was again air-dried and then treated with 2 liters of a 2% sodium hydroxide solu-

tion, allowing it to stand overnight at 20°. After filtration, the residue was washed with distilled water and the combined clear filtrates acidified with 100 cc. of concentrated hydrochloric acid. The voluminous, light yellow precipitate was filtered and washed several times by suspending it in distilled water, until the wash-water was free of hydrochloric acid. The thioglycolic acid spruce lignin was dried in a desiccator over caustic soda. The yield of crude product was 59 g. (27.5% based on dry wood). For purification 10 g. was dissolved in 90 cc. of dry dioxane, the solution centrifuged and filtered, and the lignin precipitated as a fine light cream-colored powder by dropping it into absolute ether with vigorous stirring. The product was centrifuged, washed in the centrifuge jar, twice with ether and twice with petroleum ether, and dried. After a second purification in the same way, the analytical data remained unchanged, and are in good agreement with those of Holmberg,⁵ yield 9.5 g. The product is soluble in dioxane, pyridine and cold dilute alkali, and insoluble in water, ether, petroleum ether, and benzene.

Pyridine Addition Compound.—Thioglycolic acid lignin was dissolved in absolute pyridine, the solution centrifuged and filtered, and the pyridine addition compound precipitated with ether as described above.

Phenylhydrazine Addition Compound.—To a solution of 10 g. of thioglycolic acid lignin in 40 cc. of dioxane, 10 cc. of phenylhydrazine was added and the mixture heated for two hours on a water-bath at 70–80°. After standing for two days, the solution was poured into an excess of dioxane. The reddish precipitate was centrifuged and washed with dioxane, ether, and petroleum ether. The yield was 3.2 g.; on working up the mother liquor an additional 6 g., with a somewhat lower methoxyl content, was obtained. The product was insoluble in dioxane but soluble in pyridine.

Methylation of Thioglycolic Acid Lignin with Diazomethane.—When thioglycolic acid lignin was treated with an excess of diazomethane in dioxane solution, methylation took place but the solution became very viscous, apparently because of the formation of polymerized diazomethane decomposition products which are difficult to separate from the methylated lignin derivative. The methylation was more satisfactorily carried out by passing diazomethane into the suspension of thioglycolic acid lignin in dry ether.

Diazomethane prepared from 20 cc. of *N*-nitroso-*N*-methylurethan and 40 cc. of sodium glycolate was passed into a suspension of 10 g. of purified thioglycolic acid lignin in 150 cc. of dry ether. After standing overnight, the product was dissolved in dioxane and precipitated into ether. It was centrifuged, washed twice with ether, twice with petroleum ether, and dried. The methoxyl content of the product was 24.1%. After another methylation with diazomethane from 5 cc. of *N*-nitroso-*N*-methylurethan and purification from dioxane,

(1) Part I appeared in *Ind. Eng. Chem.*, **30**, 779–781 (1938).

(2) B. Holmberg, *Svensk Papperstidn.*, **39**, Special Number, 113–114, 117–118 (1936).

(3) E. Hägglund and G. E. Carlson, *Biochem. Z.*, **267**, 467–477 (1933).

(4) K. Freudenberg, M. Meister and E. Flickinger, *Ber.*, **70**, 500–514 (1937).

(5) B. Holmberg, *Svensk Papperstidn.*, **31**, 256–258 (1928); *Ing. Vetenskaps. Akad. Handl.*, **103**, 1–75 (1930); **131**, 1–85 (1936); *Papir-J.*, **23**, 81–84, 92–96 (1935).

TABLE I
 ANALYTICAL DATA FOR LIGNIN DERIVATIVES

	C		H		S		MeO	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
1 Tetrathioglycolic acid lignin	53.2	54.6	5.5	5.3	10.1	10.1	12.5	11.7
2 Pyridine addition compound of 1	55.8	56.3	5.6	5.4	9.2	9.4	11.1	11.3
3 Phenylhydrazine addition compound of 1	8.8	8.5	10.65	10.35
4 Methylated with diazomethane	23.7	24.2
5 4 acetylated	21.0	20.65
6 4 saponified	58.3	58.05	5.84	5.85	6.0	5.5	17.4	18.5
7 1 methylated with dimethyl sulfate and sodium hydroxide	62.6	61.9	6.4	5.8	3.1	2.95	30.0	30.4
8 7 further methylated with diazomethane	62.9	62.3	6.5	6.1	32.5	32.5
9 Phenol thioglycolic acid lignin A, ether-insoluble	5.3	5.35	10.25	10.2
10 Phenol thioglycolic acid lignin B, ether-soluble	4.3	3.8	8.3	8.5

the methoxyl content was constant (24.2%). The yield was quantitative. The product is insoluble in cold dilute sodium hydroxide.

Acetylation of Thioglycolic Acid Spruce Lignin Methylated with Diazomethane.—One gram of the above product was dissolved in 10 cc. of dry pyridine, and 8 cc. of acetic anhydride was added. The mixture was allowed to stand at room temperature for forty-eight hours, after which it was centrifuged and precipitated by pouring the clear solution into ether with vigorous stirring. The acetylated product separated out as a light cream-colored powder which was washed twice with ether, twice with petroleum ether, and dried. It was then precipitated once more from its dioxane solution; yield 1.1 g.

Saponification of Thioglycolic Acid Lignin Methylated with Diazomethane.—To a solution of 4 g. of thioglycolic acid lignin methylated with diazomethane in 40 cc. of dioxane, a solution of 2 g. of sodium carbonate in 20 cc. of water was added, precipitating out a part of the lignin. The mixture was heated to 75° in a water-bath for one hour, whereupon the precipitated lignin gradually went into solution with evolution of carbon dioxide. After this, a further 2 g. of sodium carbonate in 40 cc. of water was added and a part of the dioxane distilled off under reduced pressure. The mixture was again heated to 75° for another hour, after which the rest of the dioxane was removed *in vacuo*, keeping the lignin in solution by continuous addition of water. The filtered aqueous solution was then heated for an additional half hour in a water-bath at 75°. The solution was cooled and the saponified, partially methylated thioglycolic acid lignin was precipitated by addition of a slight excess of hydrochloric acid. The orange-yellow precipitate was centrifuged and washed until the wash water was neutral toward congo red paper. The dried product was dissolved in 30 cc. of dioxane, the solution centrifuged, filtered, and the product precipitated into ether as a fine orange-yellow powder and washed in the usual way. The yield was 3.6 g. The product was soluble in dilute hydroxide solution, dioxane, and pyridine, insoluble in ether, petroleum ether, benzene, and water.

Remethylation of the saponified product with diazomethane gave a product with 23.9% MeO.

Acetylation of 3 g. of the saponified thioglycolic acid lignin in 30 cc. of dry pyridine with 25 cc. of acetic anhydride and isolation as described above gave 3.1 g. of the acetyl derivative.

Methylation of the saponified and acetylated product in ether suspension as described above gave a product with a MeO content of 19.0%.

Methylation of Thioglycolic Acid Lignin with Dimethyl Sulfate and Sodium Hydroxide Solution.—To a solution of 10 g. of thioglycolic acid lignin in 25 cc. of caustic soda solution containing 1.5 g. of sodium hydroxide, 30 cc. of 30% sodium hydroxide solution and 25 cc. of dimethyl sulfate were added drop by drop with agitation over a period of three hours, keeping the temperature at 20°. The mixture was stirred overnight and the next day the same amounts of reagents were added as before. At the end of the reaction, the methylated product was precipitated by acidifying the solution with a slight excess of hydrochloric acid and filtering. A portion of the reaction product was dissolved in a small amount of dioxane, the solution centrifuged and filtered, and the product precipitated in the usual way with ether. A methoxyl determination gave 27.4%. The main part was remethylated twice more, as before, whereupon the methoxyl content was constant. The product was then isolated and purified in the same way as the samples had been. The product was obtained as a cream-colored powder in a yield of 80%.

Further methylation of the dimethyl sulfate-methylated thioglycolic acid lignin with diazomethane was carried out by dissolving 2 g. of the dimethyl sulfate-methylated product in 20 cc. of dioxane and passing diazomethane from 4 cc. of *N*-nitroso-*N*-methylurethan into the solution. After standing overnight, the product was precipitated by dropping the filtered solution into dry ether and was then purified as usual; yield 2 g. The methoxyl content did not change after another methylation.

Action of Phenol on Thioglycolic Acid Lignin.—A solution of 8.5 g. of purified thioglycolic acid lignin in 70 g. of phenol heated to 85–90° was treated with 9 cc. of concentrated hydrochloric acid. The solution immediately became dark blue in color, but changed within a few minutes to its original brown color. The mixture was kept at 85–90° for one hour. The excess of phenol was then distilled off as far as possible under reduced pressure, leaving a dark tar. This was dissolved in about 250 cc. of a mixture of acetone and methanol (1:1). The centrifuged and filtered solution was added drop by drop to four liters of water which was vigorously stirred. The phenol thioglycolic acid lignin separated out in a colloidal state and was coagulated by the addition of a few grams of anhydrous sodium sulfate. The pinkish cream-colored precipitate

was filtered, washed with water, and dried. The yield was 9.6 g. A methoxyl determination gave 9.4%.

The crude product obtained above was dissolved in dry dioxane to give a 10% solution and the ether-insoluble compound was precipitated by dropping the solution into dry ether. It separated as a light buff-colored powder. This purification was repeated twice more. The yield was about 70%.

The combined ether-dioxane mother liquors were distilled to dryness—toward the end, under reduced pressure. The resinous residue was extracted with 250 cc. of absolute ether, leaving a small amount of a resin. The ether solution, after standing overnight whereby a very small amount of resin was deposited on the glass walls, was filtered and again evaporated to dryness. The residue was taken up in 25 cc. of absolute methanol and dropped into 600 cc. of distilled water with stirring. The ether-soluble phenol thioglycolic acid lignin separated out as an almost white powder, which on drying became slightly pinkish. The yield was approximately 25% of the crude phenol thioglycolic acid lignin.

Discussion

The original thioglycolic acid lignin gives a bright purple color with Wiesner's reagent (phloroglucinol and hydrochloric acid), a behavior previously observed by Holmberg. Diazomethane-methylated thioglycolic acid lignin does not yield this typical color. This fact is in agreement with the earlier observation⁶ that a hydroxyl group in the lignin molecule is responsible for the coloration. When this hydroxyl group is methylated with diazomethane, the reaction between phloroglucinol and lignin can no longer occur. Since many lignin preparations, prepared by entirely different methods, react with Wiesner's reagent but fail to do so after methylation with diazomethane, the long-debated question, as to whether the coloration is a typical reaction of lignin itself or is due to a small amount of a by-product, may be definitely decided in favor of the first conception.

When acetic anhydride is added to a solution of thioglycolic acid lignin in pyridine and the mixture is kept at room temperature, it soon changes into a gel which is no longer soluble in organic solvents. However, the acetylation of thioglycolic acid lignin premethylated with diazomethane gives an acetylated product, easily soluble in dioxane. This may indicate that, in the acetylation of the unmethylated thioglycolic acid lignin, the free carboxyl groups of the thioglycolic acid lignin may form anhydrides or lactone, in this way making the product insoluble.

(6) F. E. Brauns and D. S. Brown, *Ind. Eng. Chem.*, **30**, 779-781 (1938).

According to Holmberg's theory, the carboxyl group of the thioglycolic acid in thioglycolic acid lignin remains free. These groups may be methylated by diazomethane with the formation of methyl esters. Unlike methyl ether groups, these methyl ester groups should be saponifiable. However, when diazomethane-methylated thioglycolic acid lignin was subjected to a mild saponification with sodium carbonate, not only the methyl ester groups but a part of the thioglycolic acid groups are split off.

Methylation of thioglycolic acid lignin with dimethyl sulfate and sodium hydroxide also results in a splitting off of thioglycolic acid groups, yielding a product with 30.4% MeO and 2.95% sulfur. Its solubility in cold dilute sodium hydroxide solution indicates that the product still contains some free carboxyl groups. This is also shown on methylation with diazomethane, whereby the methoxyl content increases to 32.5% and the product becomes insoluble in cold dilute caustic soda.

Since it has been found that lignin sulfonic acid reacts with phenol to give phenol lignin sulfonic acid,⁷ it was of interest to study the behavior of the thioglycolic acid lignin toward phenol under the same conditions as those used for the preparation of phenol spruce lignin.⁸ The crude phenol thioglycolic acid lignin was separated into an ether-insoluble (A) and an ether-soluble (B) fraction, which differ in their elementary analysis. In both cases a part of the thioglycolic acid is replaced by the phenol group. Unfortunately, the data on the phenol lignin sulfonic acid are very meager, and a comparison of this derivative with phenol thioglycolic acid lignin cannot be made.

The composition of thioglycolic acid lignin from spruce will not be discussed in detail, but reference may be made to Holmberg's⁵ work. Since the empirical formula, $C_{47}H_{52}O_{16}$, for a spruce lignin unit has been proposed by Brauns and Hibbert⁹ it is interesting to compare this formula with that of thioglycolic acid lignin. Holmberg¹⁰ gives the composition of the demethylated parent substance (based on C_9) of the Brauns formula as $C_9H_9O_{3.43}$, which compares well with that of his formula, $C_9H_9O_{3.5}$. From the analytical results of carefully purified thioglycolic acid lignin,

(7) C. Dorée and L. Hall, *J. Soc. Chem. Ind.*, **44**, 270T (1925).

(8) I. K. Buckland, F. E. Brauns and H. Hibbert, *Can. J. Research*, **B13**, 61-67 (1935).

(9) F. E. Brauns and H. Hibbert, *THIS JOURNAL*, **55**, 4720 (1933); *Can. J. Research*, **B13**, 28-34 (1935).

(10) Holmberg, *Papier Fabrikant*, **36**, No. 24-25, 218-223 (1938).

it is found that four thioglycolic acid molecules react with one molecule of lignin of the above formula, to give tetrathioglycolic acid spruce lignin¹¹ of the composition of $C_{42}H_{32}O_6(OCH_3)_5(OH)_5(HSCH_2COOH)_4$.

The analytical data in Table I show that, on saponification of the diazomethane-methylated tetrathioglycolic acid lignin, in addition to the ester methoxyl groups, two thioglycolic acid groups have been split off, giving a partially methylated dithioglycolic acid lignin of the formula $C_{42}H_{32}O_6(OCH_3)_6(OH)_4(HSCH_2COOH)_2$. Thus, it is seen that no new phenolic hydroxyl groups have been formed, in spite of the entrance of four thioglycolic acid groups into the lignin unit.

Methylation of thioglycolic acid with dimethyl sulfate and sodium hydroxide solution causes the methoxyl content to increase to 30.0%, while the sulfur content decreases from 10.1 to 3%. For a monothioglycolic acid lignin, based on the above formula for the lignin unit, the formula $C_{42}H_{32}O_6(OCH_3)_{10}(HSCH_2COOH)$ is obtained, the calculated analytical data of which are in good agreement with the found values.

The fact that, on mild saponification of the diazomethane-methylated product, four methoxyl groups are split off indicates that these groups are present in ester form, and that the thioglycolic acid must have reacted, as already assumed by Holmberg, through its mercapto group. If this group reacts with a hydroxyl group of the lignin with ether formation by elimination of water it should be stable toward alkali. However, the fact that the diazomethane-methylated thioglycolic acid lignin can be acetylated and that its calculated methoxyl content agrees with that of a tetraacetyl-tetrathioglycolic methyl ester lignin, is in disagreement with the assumption that all four thioglycolic acid groups have reacted with hydroxyl groups of the lignin. It may be possible, though, that one thioglycolic

acid molecule has reacted with the same hydroxyl group of the lignin unit which reacts with alcohols and phenol with ether formation. This is supported by the fact that ethyl lignin, in which the hydroxyl group in question is protected by the ethoxyl group, reacts with three thioglycolic acid groups only.¹² Fully methylated glycol lignin reacts with thioglycolic acid in the same manner.¹³ The determination of the methoxyl content is not accurate enough to decide this question. It is interesting, however, that the number of phenol groups and the number of thioglycolic groups which react with spruce lignin to form phenol lignin A⁸ and thioglycolic acid lignin, respectively, are in both cases the same, namely, four. It is also of interest that, in the action of phenol with thioglycolic acid lignin, two thioglycolic acid groups are replaced by two phenol groups. Since, however, the mechanism of reaction between phenol and lignin is still unknown, no conclusions can be drawn with regard to the formation of tetrathioglycolic acid lignin.

Summary

Thioglycolic acid spruce lignin has been methylated (a) with diazomethane, (b) with dimethyl sulfate and sodium hydroxide, and (c) with dimethyl sulfate followed by diazomethane. Saponification of the diazomethane-methylated thioglycolic acid lignin, as well as the methylation with dimethyl sulfate, resulted in the splitting off of a part of the thioglycolic groups. The results of the investigation do not indicate that, with the entrance of each thioglycolic group into the lignin molecule, a new hydroxyl group is formed, nor that a hydroxyl group of the lignin has disappeared. On reaction of thioglycolic acid lignin with phenol, a part of the thioglycolic groups is replaced by a phenol group.

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(12) B. Holmberg, *Svensk. Kem. Tid.*, **47**, 257-265 (1935).

(13) Unpublished work.

(11) This term has already been used by Holmberg.⁵