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THE REACTION OF METHYL HYPOCHLORITE WITH LIGNIN

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THE REACTION OF METHYL HYPOCHLORITE WITH LIGNIN[1]

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Lignin reacts with chlorine in methanol solution to give a product containing a higher methoxyl content than would be expected if the methanol did not enter the reaction. Since some methyl hypochlorite will be formed by the action of chlorine on methanol, it was thought that methyl hypochlorite, which is known to add to ethylenic linkages (1, 2), had added to ethylenic linkages in lignin. If this reaction were quantitative, it might be used to determine the number of ethylenic linkages in lignin.

This paper covers a study of the reaction of lignin with methyl hypochlorite prepared by different methods.

Experimental

Chlorination of lignin in methanol.--Five grams of dried lignin was suspended in dried methanol, the mixture was cooled to and maintained at 10°; dried chlorine was introduced until no further change in the color of the resulting product was evident. During the reaction lignin, which was not previously dissolved, went into solution. The mixture was poured on crushed ice and washed with ice water until the wash water gave no test with starch-iodide paper. The product was dried in a vacuum at room temperature. Table 1 shows the composition of various lignins which have been treated with chlorine in methanol; yield approximately 6.5 g.

Chlorination of lignin in methanol in the presence of barium carbonate.--Five grams of dried lignin was mixed with 200 cc. of dried methanol and 25 g. of anhydrous barium carbonate added. While stirring and cooling the mixture to 10°, dried chlorine was introduced until no further change was evident. The mixture was filtered to remove the excess barium carbonate and then poured on crushed ice, which precipitated the lignin derivative as a light yellow powder. This powder was then recovered on a Büchner filter and washed with ice water until free from chlorine. The product was first air dried on the filter and then dried in vacuum. The yield of chlorinated material was approximately 5.8 g.

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Table 2 gives the methoxyl and chlorine content of the lignins treated.

Lignin treated with dichlorourea and methanol.--Three grams of the most soluble fraction of maple methanol lignin (3), which contained 27 percent methoxyl, was dissolved in 200 cc. of methanol which had been dried over drierite and distilled. To this solution dried dichlorourea, prepared according to the method of Chattaway (4), was added in varying amounts and allowed to stand for about 1 hour. The solution was poured on 400 g. of crushed ice and agitated. The precipitate was washed with ice water until the wash water showed no reaction for chlorine. The product was dried for a short time by drawing air through it on a Büchner funnel and then dried in vacuum. Table 3 contains the methoxyl and chlorine contents of methanol lignin treated with varying amounts of dichlorourea at different temperatures. The yield of chloro compounds ranged from 3.3 to 3.8 g. depending on the temperature and the chlorourea used.

The action of methyl hypochlorite on lignin.--A solution of methyl hypochlorite in carbon tetrachloride was prepared according to the method of Taylor, McMullen and Gammal (5). Two hundred cubic centimeters of this solution containing approximately 5 g. of methyl hypochlorite was added to a mixture containing 5 g. of lignin in 200 cc. of methanol while stirring and cooling. The stirring was continued for an hour after the methyl hypochlorite solution had been added. The solvent was evaporated at room temperature by distillation in vacuum, using a water pump, until about 50 cc. remained. The concentrated solution was added to 1 liter of petroleum ether (b.p. 80-100°), which precipitated the lignin derivative as a flocculent powder. The powder was filtered from the solution and washed with petroleum ether until the filtrate gave no reaction for chlorine. The yield of chlorolignin ranged from 5.5 to 6.5 g. Table 4 gives the methoxyl and chlorine content of the lignins treated.

Results and Discussion

From table 1 it may be noted that the reaction of chlorine with lignin in methanol gave a product containing more methoxyl than the original lignin. Isolated lignin was used for this study so that any increase in methoxyl was due to reaction during the chlorination and not previous to the chlorination, as stated by Jansen and Bain (6), who also observed an increase in the methoxyl content of lignin obtained by the chlorination of wood in methanol. The amount of chlorine taken up by isolated spruce lignin when chlorinated in methanol was approximately the same as that found by Jansen and Bain, who chlorinated spruce wood and extracted the lignin derivative. Their product contained 15.9 percent methoxyl and 35.6 percent chlorine, as compared

with 16.8 percent methoxyl and 34.1 percent chlorine in this report. Isolated lignin took up a slightly greater amount of methoxyl than combined lignin. The greater absorption of methoxyl with isolated lignin may be due to conditions being more favorable for the reaction. It is apparent that a part of the chlorine adds to lignin as methyl hypochlorite. In table 1, using approximately 950 which has been referred to previously (7) as a unit weight for lignin to be treated, it is shown that maple lignin (with a methoxyl content of 20.6 percent), methanol maple lignin (with a methoxyl content of 27 percent), and methanol spruce lignin (with a methoxyl content of 20.4 percent) have taken on, during the chlorination, two methoxyl groups each while spruce lignin (with a methoxyl content of 17 percent) has taken up three. This would account for the presence of two ethylenic linkages in the samples of maple lignin and three such linkages in spruce lignin having a methoxyl content of 17 percent, if methyl hypochlorite is added to these bonds. Chlorine other than that in the methyl hypochlorite reacted with the lignin, giving a product with a high chlorine content.

Referring to table 2, if barium carbonate is added to the chlorinating mixture, the chloride ion would be removed and substitution reactions would be largely eliminated because most of the chlorine would be present as the hypochlorite. In methanol solution this would be present as methyl hypochlorite. Table 2 gives the composition of lignin chlorinated at 10° in the presence of barium carbonate. In this reaction less chlorine was found in the lignin derivatives than that shown in table 1, but the amount was still in excess of the amount that would be present if the entire reaction were due to the addition of methyl hypochlorite. The increase in methoxy content was the same as that shown in table 1. In this table it is shown that fully methylated maple lignin adds two methoxyls and therefore it is apparent that methylation does not change the degree of unsaturation of the lignin molecule.

When working with phenylethylene, Alpatov (8) found that dichlorourea in methanol produced methyl hypochlorite which added to the double bond of phenylethylene to produce α-phenyl, α-methoxy, and β-chloroethylene. This method of determining the presence of double bonds was applied to the most soluble fraction of methanol maple lignin containing 27 percent methoxyl. Table 3 shows the composition of methyl hypochlorite addition compounds produced by treating this lignin with dichlorourea in methanol. However, in each case chlorine in excess of that in the methyl hypochlorite also reacted with the lignin. Temperature ranges from 5° to 20° had very little effect on the reaction. At 30° the reaction proceeded as if free chlorine were added to the methanol solution of lignin. The same amount of methoxyl was added if 3, 7 or 15 g. of dichlorourea were added but the amount of chlorine introduced increased with the increase in quantities of dichlorourea. The methoxyl groups in the lignin unit of 950 weight increased from 8 to 10, showing evidence of two ethylenic groups.

Table 4 contains the composition of lignin samples treated with a carbon tetrachloride solution of methyl hypochlorite. At 10° results similar to those obtained with dichlorourea were obtained. The products obtained at 25° indicated that the methyl hypochlorite must have decomposed and then reacted as free chlorine.

Conclusions

Lignin reacts with chlorine in methanol to produce compounds containing more methoxyl than the starting material.

Methyl hypochlorite prepared in various ways reacts with maple lignins to produce compounds containing two methoxyl groups in excess of those of the starting material and with various spruce lignin samples to produce compounds with two or three methoxyl groups in excess of the starting material.

The addition of these methoxyl groups indicates the presence of two ethylenic groups in maple lignin and two or three, depending on the derivative, in spruce lignin.

Literature Cited

1. P. D. Bartlett and D. S. Tarbell. Jour. Amer. Chem. Soc. 58:466 (1936).

2. E. L. Jackson. Jour. Amer. Chem. Soc. 56:977 (1934).

3. E. E. Harris. Report presented before the American Chemical Society, Pittsburgh, Pa., 1936, unpublished.

4. F. O. Chattaway. Chem. News 98:285 (1909).

5. M. C. Taylor, R. B. McMullen and C. A. Gammal. Jour. Amer. Chem. Soc. 47:395 (1925).

6. G. V. Jansen and J. W. Bain. Can. J. Research 15:279 (1937).

7. E. E. Harris. Jour. Amer. Chem. Soc. 58:894 (1936).

8. D. M. Alpatov. Acta Univ. Voronegiensis 3:172 (1937).

Table 1.--Composition of lignin chlorinated in methanol at 10° C.

Material	Before treatment	After treatment		
	Methoxyl	Methoxyl	Chlorine	Approximate ratio of groups MeO/Cl
	Percent	Percent	Percent	
Maple lignin[1]	20.6	16.6	33.4	8/14
Methanol maple lignin[2]	27.0	21.3	32.0	10/14
Spruce lignin[1]	17.0	16.8	34.1	8/14
Methanol spruce lignin[3]	20.4	17.1	33.8	8/14

[1] Prepared by sulfuric-acid method.

[2] The most soluble fraction of methanol lignin.

[3] The less soluble fraction of methanol lignin.

Table 2.--Composition of lignin chlorinated in methanol at 10° C. in the presence of barium carbonate

Material	Before treatment		After treatment			
	Methoxyl		Methoxyl	Chlorine	Approximate ratio of groups MeO/Cl	
	Percent	(2)	Percent	Percent		
Maple lignin	20.6	(6 MeO)	20.7	17.7	8/6	
Methylated maple lignin[1]	32.3	(10 MeO)	27.8	16.9	12/6	
Methanol maple lignin	27.0	(8 MeO)	24.5	16.8	10/6	
Spruce lignin[1]	17.0	(5 MeO)	19.7	19.0	8/7	
Methanol spruce lignin	20.4	(6 MeO)	24.0	19.8	9/7	

[1] These values were obtained from an unpublished report by R. L. Mitchell, Forest Products Laboratory, Project 285.

[2] These values are based on a lignin unit weight of approximately 950.

Table 3.---Methanol maple lignin treated with dichlorourea in methanol solution

Temperature	Amount of urea used	Before treatment	After treatment		
		Methoxyl	Methoxyl	Chlorine	Approximate ratio of groups MeO/Cl
° C.	Grams	Percent	Percent	Percent	
5	3	27	26.8	11.9	10/4
5	7	27	26.7	14.43	10/5
5	15	27	25.4	17.9	10/6
10	3	27	27.8	13.15	10/4
10	7	27	26.5	14.8	10/5
10	15	27	26.2	16.2	10/6
15	3	27	27.6	13.38	10/4
15	7	27	26.5	14.8	10/5
15	15	27	25.3	17.2	10/6
20	3	27	25.8	13.1	10/4
20	7	27	27.1	15.0	10/5
30	7	27	23.0	30.0	10/14

Table 4.--Composition of lignin treated with methyl hypochlorite in methanol

Material	Temperature of treatment	Before treatment	After treatment		
		Methoxyl	Methoxyl	Chlorine	Approximate ratio of groups MeO/Cl
	° C.	Percent	Percent	Percent	
Methanol maple lignin ...	10	27.0	25.1	17.0	10/6
Maple lignin	10	20.6	20.8	17.9	8/6
Maple lignin	25	20.6	17.9	28.8	8/10
Methanol spruce lignin ..	10	20.4	23.7	20.0	9/7
Spruce lignin	25	16.8	13.3	31.1	6/12
Spruce lignin	10	16.8	20.7	19.4	8/7