in the literature, but Steacie and Elkin[13] have observed that lead above the melting point is even more active in promoting the decomposition of methyl alcohol than solid lead of equal gross surface area. Hartman and Brown[14] found also that the catalytic efficiency of cadmium in reduction of nitrobenzene is little affected by melting.

In our own experiments, there is the possibility of reactions between the adsorbate and substances in the vapor phase. When the pressure of reactant halide approaches one atmosphere, the mechanism may include such additional reactions as $CH_2 + CH_2Cl_2\ (g) \xrightarrow{(Na)} CH_4 + C + NaCl$. This reaction accounts stoichiometrically for a reduction in the production of hydrogen and an increase in the production of methane at higher pressures of halide.

On metals, other than sodium, chemisorption of aliphatic free radicals seems to have been observed by other authors. For example, in the presence of reduced nickel, a metal which normally promotes hydrogenation, the decomposition products from a mixture of hydrogen and methylene chloride at 200° are carbon and hydrogen chloride.[15] Chloroform and hydrogen give the same products.

Tollens[16] identified hydrogen, acetylene, ethylene, ethane and chloroethylene in products from the reaction of ethylidene chloride and sodium in the temperature range 180–200°. We have found the products at 320° to be carbon, hydrogen and methane as well as the C_2 gases. A similar difference is found when chloroform is the reactant. At 320°, the CH radicals resulting from the initial chloroform and sodium reaction are adsorbed in an activated state. The most important stable products are carbon and hydrogen. At lower temperatures, chloroform and potassium amalgam are a source of acetylene,[17] as are chloroform and copper.[18] The effect of temperature on the equilibria at the surface would account for the different proportions of products.

Summary

Carbon, hydrogen and methane with smaller amounts of ethane, ethylene and acetylene are the principal products formed by passing methylene chloride or chloroform into molten sodium over a fairly wide range of temperatures and pressures.

A series of reactions between free radicals adsorbed in an activated state on the surface of the metal is suggested as source of the products.

NEW YORK, N. Y. RECEIVED OCTOBER 16, 1944

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[14] Hartman and Brown, *J. Phys. Chem.*, **34**, 2651 (1930).

[15] Sabatier and Mailhe, *Compt. rend.*, **138**, 408 (1904).

[16] Tollens, *Ann.*, **137**, 311 (1866).

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[CONTRIBUTION FROM THE INSTITUTE OF PAPER CHEMISTRY]

Acetic Acid Spruce Lignin and Acetic Acid Willstätter Spruce Lignin[1]

BY F. E. BRAUNS AND M. A. BUCHANAN

Lignin can be extracted from wood by organic acids in the presence of small amounts of mineral acid as a catalyst. In 1916, Pauly[2] described the delignification of wood by means of acetic acid in the presence of sulfuric acid and in 1921 Pauly and Foulon[3] isolated lignin with 85% acetic acid containing 0.3% sulfuric acid. Routala and Sevón[4] reported in 1927 that glacial acetic acid containing a trace of hydrochloric acid dissolved at least a part of the lignin which they isolated by pouring the acetic acid solution into water. The lignin had a methoxyl content of 14.6%. A year later, Friedrich[5] isolated lignin in a similar way, but the lignin, after purification from alcohol and water, had a methoxyl content of only 10.5%, from which it was concluded that considerable acetylation had taken place. After saponification with sodium hydroxide and purification of the crude lignin by dissolving it in chloroform and reprecipitating it with ether, a lignin with 14.4 to 14.6% methoxyl was obtained.

Schütz and Knackstedt[6] recently described the extraction of lignin from wood by means of acetic acid with magnesium chloride as a catalyst. This mixture was used also by Freudenberg and Plankenhorn[7] who claimed that, by repeated extraction, almost the entire lignin can be brought into solution and that the various fractions do not differ in their chemical composition. The acetic acid lignin obtained by Freudenberg had a methoxyl content of 13.2% and an acetyl content of 10.2%, corresponding to 2 acetyl groups per lignin building unit.[8] After saponification, the methoxyl increased to 14.6%. On treatment with 72% sulfuric acid, Freudenberg's acetic acid lignin lost 21.2% in weight, of which 10.2% was due to acetyl groups split off and 11% to solubility of carbohydrate material. The methoxyl content of

[1] This paper was presented at the New York, N. Y., meeting of The American Chemical Society, September 11, 1944.

[2] Pauly and Aktiengesellschaft für Zellstoff u. Papierfabrikation, German Patent 309,551 (June 20, 1916).

[3] Pauly, Foulon, *et al.*, *Ber.*, **67**, 1177 (1934).

[4] Routala and Sevón, *Ann. Acad. Sci. Fennicae*, **29A**, No. 11, 48 (1927).

[5] Friedrich, *Z. physiol. Chem.*, **176**, 127 (1928).

[6] Schütz and Knackstedt, *Cellulosechem.*, **20**, 15 (1942).

[7] Freudenberg and Plankenhorn, *Ber.*, **75**, 857 (1942).

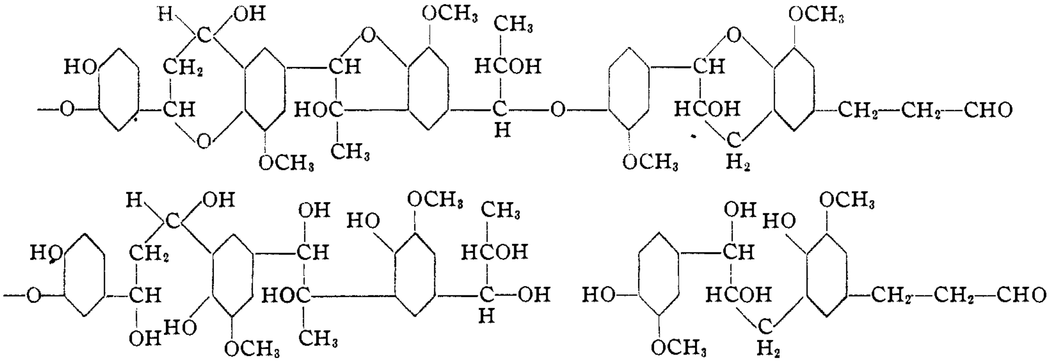
[8] Brauns, THIS JOURNAL, **61**, 2120 (1939).

the acetyl and carbohydrate-free lignin was calculated to be 16.6%, a methoxyl content often found for a Klason spruce lignin. The content of phenolic hydroxyl groups of saponified acetic acid lignin was found to be 2.1%, which corresponds to one phenolic hydroxyl group per lignin building unit. The phenolic hydroxyl content of cuproxam lignin is only 0.75%.

In a recent paper, Pauly[9] claimed that, by the action of acetic acid in the presence of 0.3% sulfuric acid, all the lignin goes into solution and that all the ether linkages, except the methoxyl ether linkages, are split with the formation of a product with a high phenolic hydroxyl content. For this reason, he termed these products acetic acid "lignols" instead of lignin.

Discussion

If ether linkages in the lignin molecule are split on extraction of the lignin from wood with acetic acid in the presence of mineral acid or magnesium chloride, then acetic acid spruce lignin should have a higher hydroxyl content than isolated native spruce lignin.[8] On the basis of Freudenberg's formula, in which the lignin building stones C_6–C_3 are linked together through the side-chain by furan or pyran ring formation and by ordinary ether linkages, then, by the opening of these heterocyclic rings and the splitting of the ordinary ether linkages, a new alcoholic and a new phenolic hydroxyl group should be formed for each lignin building stone.



An increase in the number of phenolic hydroxyl groups should be detected on methylation with diazomethane, which should give a partially methylated acetic acid lignin with a methoxyl content higher than that of the corresponding native lignin derivative. The new aliphatic hydroxyl groups should be detected on complete methylation with dimethyl sulfate and the fully methylated acetic acid spruce lignin should have a considerably higher methoxyl content than the corresponding native lignin derivative. A higher hydroxyl content of acetic acid spruce lignin should also be detected by acylation. To study this question, acetic acid lignin has been prepared from black spruce in three fractions by three successive extractions and from Willstätter black spruce lignin, and has been compared with the native lignin of the same wood.

On treatment of the three acetic acid lignin fractions with 72% sulfuric acid, carbohydrate and acetyl groups are split off and Klason lignins are obtained in 84.3, 88.6, and 90% yields, respectively, with methoxyl contents of 14.7, 14.6, and 13.5%.

Carefully prepared hydrochloric acid lignin with a methoxyl content of 15.5% is completely soluble when heated with acetic acid in the presence of magnesium chloride. The acetic acid Willstätter lignin has a methoxyl content of 14.6%, which agrees very well with that of Freudenberg's acetic acid cuproxam lignin (14.7%). The latter, however, contained 8% hexosans. When the methoxyl content is corrected to a hexosan-free basis, it becomes 16.0%. Because the Willstätter lignin is free of carbohydrate material, the acetic acid Willstätter lignin is also free of it. In spite of this, acetic acid Willstätter lignin, when treated with 72% sulfuric acid, is recovered in 87.14% yield only and the Klason lignin obtained from it has a methoxyl content of 16.0%. The decrease in methoxyl from 15.5% to 14.6% when Willstätter lignin is dissolved in acetic acid is caused by partial acetylation because, on saponification of acetic acid Willstätter lignin, the methoxyl content again increases to 15.7%.

The methoxyl values of acetic acid spruce lignin, acetic acid Willstätter spruce lignin, isolated native spruce lignin, and their derivatives are given in Table I. These data show that the methoxyl content of acetic acid Willstätter lignin (14.6%) agrees quite well with that of isolated native spruce lignin (14.8%). This, however, is incidental because the acetic acid Willstätter lignin contains 8.5% acetyl. On saponification, the methoxyl content increases to 15.6%, which is the same as that of the original Willstätter lignin. The methoxyl content of the acetic acid spruce lignin obtained by direct extraction from sprucewood is about 2% lower than that of native lignin as a result of partial acetylation and the presence of about 5% carbohydrate material. On saponification, the methoxyl content of acetic acid lignin increases from 12.6 to 14.1%.

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(9) Pauly, *Ber.*, **76**, 864 (1943).

TABLE I

		Acetic acid spruce lignin				Acetic acid Willstätter spruce lignin				Isolated native spruce lignin			
			Number of OR groups with R =				Number of OR groups with R =				Number of OR groups with R =		
No.	Lignin derivative	MeO, % (S, %)	Me	Acyl	H	MeO, % (S. %)	Me	Acyl	H	MeO, % (S, %)	Me	Acyl	H
1	Original lignin	12.6	4	2 AcO	3	14.5	4	2 AcO	3	14.8	4	0	4 1 enol
2	Saponified lignin	14.1	4	0	5	15.6	4	0	5	..	..	....	...
3	No. 1 treated with 72% H_2SO_4	14.8	..	....	..	16.0	..	....	..	15.5	..	....	...
4	No. 1 acetylated	10.9	4	5?	0	12.8	4	5 AcO	0	11.8	4	5 AcO	0
5	No. 1 toluenesulfonated	9.2 (7.1)	4	2 AcO 3 tosyl	0	9.4 (7.2)	4	2 AcO 3 tosyl	0	7.3 (9.95)	4	5 tosyl	0
6	No. 2 toluenesulfonated	7.6 (9.1)	4	4 tosyl	1?	8.6 (9.2)	4	4 tosyl	1?	..	..	....	...
7	No. 1 methylated with CH_2N_2	17.4	5	2 AcO	2?	21.0	6	2 AcO	1	21.4	6	0	3
8	No. 2 methylated with CH_2N_2	21.0	6	0	3?	24.4	7	0	2	..	..	....	...
9	No. 7 toluenesulfonated	..	..	....	..	16.9 (3.6)	6	2 AcO 1 tosyl	0	12.3 (6.9)	6	3 tosyl	0
10	No. 8 toluenesulfonated	..	..	....	..	16.7 (5.3)	7	2 tosyl	0	..	..	....	..
11	No. 7 methylated with Me_2SO_4	30.1	9	....	...	30.5	9	0	0	31.3	9	0	0
12	No. 1 methylated with MeOH-HCl	13.6	6	2 AcO	2?	13.7	6	2 AcO	2?	20.3	6	0	4

The methoxyl content (10.9%) of the acetylated acetic acid lignin is about 1% lower than that of the corresponding acetylated isolated native spruce lignin. As the former still contains carbohydrate material which may also be acetylated, no calculation can be made as to the number of acetyl groups present. On acetylation of the acetic acid Willstätter spruce lignin, three acetyl groups enter the lignin building unit, in addition to the two acetyl groups already present; on acetylation of isolated native spruce lignin, five acetyl groups are introduced.

On toluenesulfonation of isolated native lignin, five tosyl groups are introduced into the lignin building unit; on toluenesulfonation of acetic acid Willstätter lignin, only three tosyl groups enter the lignin building unit because two hydroxyl groups have already been esterified by acetyl groups. The agreement of the methoxyl content and of the tosyl group content of acetic acid spruce lignin with that of acetic acid Willstätter spruce lignin may be incidental or it may be that the carbohydrate material was removed during the toluenesulfonation. On toluenesulfonation of the two saponified lignins, only a little more than four tosyl groups are introduced into the lignin building unit, instead of the expected five groups. An investigation of this discrepancy is under way.

Methylation of isolated native spruce lignin[8] with diazomethane causes the formation of two new methoxyl groups in the lignin building unit, bringing the number up to six. When the unsaponified acetic acid Willstätter lignin is methylated with diazomethane under anhydrous conditions, here, too, two hydroxyl groups are methylated, bringing the number of methoxyl groups up to six. On methylation of the unsaponified acetic acid lignin, however, only one hydroxyl group is methylated, bringing its number up to five. Diazomethane methylation of the saponified acetic acid lignin, on the other hand, causes the introduction of two new methoxyl groups, the same as the diazomethane methylation of isolated native spruce lignin. When, however, the saponified acetic acid Willstätter spruce lignin is methylated with diazomethane, three hydroxyl groups are methylated, bringing the number of methoxyl groups up to seven. In both acetic acid lignins, therefore, one hydroxyl group capable of being methylated with diazomethane is present in the original acetic acid lignin in an acetylated state which prevents its methylation before hydrolysis. Unlike isolated native spruce lignin, *saponified acetic acid Willstätter spruce lignin possesses three slightly acidic hydroxyl groups.* Since the total number of OR groups is the same in the acetic acid Willstätter lignin as in the other lignins, the Willstätter lignin must have been changed during its conversion into the acetic acid compound so that one aliphatic hydroxyl group has disappeared and a phenolic or enolic hydroxyl group has been formed. That the total number of OR groups in the acetic acid Willstätter lignin is unchanged is shown by toluenesulfonation of the two diazomethane-methylated compounds. Only one toluenesulfonyl group is introduced into the diazomethane-methylated unsaponified acetic acid Willstätter lignin, which brings the total number of OR groups to nine, that is, six methoxyl, two acetyl, and one tosyl, whereas toluenesulfonation of the diazomethane-methylated saponified acetic acid Willstätter lignin gives a product with two tosyl groups, which brings the total number of OR groups again to nine. Toluenesulfonation of the diazomethane-methylated isolated native lignin gives a product with three tosyl groups, which again brings the total number of OR groups in the lignin building unit up to nine.

Methylation of the three lignins with dimethyl sulfate and sodium hydroxide results in completely methylated products with simultaneous saponification of the acetyl groups. The methylated products each have nine methoxyl groups per lignin building unit.

When the two acetic acid lignins are treated with absolute methanol containing 0.5% hydrogen chloride, methanol lignins are formed with two new methoxyl groups, as is the case with isolated native lignin. Since, in the latter case, the two newly added methoxyl groups are split off again on treatment with mineral acid, they are present as acetal methoxyl. No attempt has been made, as yet, to prove that the newly formed methoxyl groups in the methanol lignins from the acetic acid lignins are present in an acetal-like form but, since Freudenberg[7] found some indications that his acetic acid lignin contains about one carbonyl group per lignin building unit, it is very probable that the methanol lignin obtained from the acetic acid lignin contains the two new methoxyl groups also in an acetal form. An investigation in this direction is under way.

These results show that neither in the isolation of lignin from spruce by acetic acid nor during the conversion of Willstätter spruce lignin into acetic acid lignin is the number of hydroxyl groups in the lignin building unit changed.

Experimental Part

Preparation of Acetic Acid Spruce Lignin.—Sprucewood sawdust (equivalent to 475 g. of air-dry material; moisture content, 7.9%), previously extracted with alcohol and benzene-alcohol (1:1), was refluxed for ten hours with a mixture of 1900 cc. of glacial acetic acid and 25 g. of $MgCl_2 \cdot 6H_2O$ dissolved in 100 cc. of water. After cooling, about 800 cc. of the liquor was drained off and filtered through a sintered glass funnel. The residual wood was washed by heating with 1500 cc. of 95% acetic acid for two hours, after which the supernatant liquor was drained off and filtered. The combined extract and washings were concentrated under reduced pressure to a sirup (Fraction A). The residual wood was refluxed for ten hours with a mixture of 18 g. of $MgCl_2 \cdot 6H_2O$ in 1200 cc. of glacial acetic acid and 65 cc. of water. The mixture was filtered and the residual wood was washed with 95% acetic acid as before. The filtrate and the washings were concentrated *in vacuo* (Fraction B). A third extraction was made with 1200 cc. of glacial acetic acid and 21 g. of $MgCl_2 \cdot 6H_2O$. The residual wood meal was filtered, washed with one liter of glacial acetic acid and 500 cc. of dioxane, and extracted in a Soxhlet apparatus with dioxane. The acetic acid and the dioxane solutions were concentrated separately under reduced pressure and the residues were combined (Fraction C). The residual pulp contained 7.7% lignin (determined as Klason lignin) and had a methoxyl content of 12.3%.

Fractions A, B, and C were each dissolved in 90% dioxane to give approximately 8-10% solutions. The solutions were centrifuged and filtered and the lignin was isolated by dropping the solutions into large amounts (10-12 liters each) of distilled water. The lignin partially separated as a fine flocculent precipitate and partially remained in colloidal solution. This solution was coagulated by the addition of a few grams of anhydrous sodium sulfate, after which the lignin could be filtered easily. The precipitates were washed with distilled water and dried in a desiccator over sulfuric acid and sodium hydroxide. The yields of crude lignin were 54, 43, and 16 g., with methoxyl contents of 12.1, 12.3, and 11.9%, respectively. The lignins were purified by dissolving them in anhydrous dioxane to give 8-10% solutions, centrifuging and filtering the solutions, and precipitating the lignins by dropping the solutions into anhydrous ether or benzene. The lignins were washed with ether or benzene and petroleum ether and dried. The analyses of the purified acetic acid lignins and of their derivatives are given in Tables I and II.

Table II

Analyses of the Acetic Acid Lignins and their Derivatives

		C	H	MeO	AcO
1	Acetic spruce lignin first fraction	63.13	5.47	12.6	11.6
2	Acetic spruce lignin second fraction	64.18	5.35	12.9	10.5
3	Acetic spruce lignin third fraction	64.5	5.28	12.0	9.4
4	No. 1 saponified	64.6	5.5	14.1	..
5	Acetic acid Willstätter lignin	65.3	5.45	14.5	8.6
6	No. 5 saponified	65.2	5.6	15.6	..
7	No. 1 fully methylated	66.3	6.4	30.1	..
8	No. 5 fully methylated	67.1	6.4	30.5	..

The acetyl derivative (23.7% AcO) of acetic acid lignin from Fraction A was prepared by treating the lignin with acetic anhydride in pyridine solution.

The toluenesulfonyl derivative of acetic acid spruce lignin was prepared by treating a solution of 1 g. in 10 cc. of anhydrous pyridine with 3 g. of *p*-toluenesulfonyl chloride at room temperature for 24 hours and then heating the mixture for 0.5 hour at 70°. The mixture was poured onto cracked ice and the precipitated lignin derivative was filtered, washed, dried, and purified by dropping its solution in dioxane into anhydrous ether, washing with ether and petroleum ether, and drying the product in an Abderhalden over phosphorus pentoxide at 100°.

Methylation of Acetic Acid Spruce Lignin with Diazomethane.—A solution of 10 g. of acetic acid spruce lignin (first fraction) in 100 cc. of anhydrous dioxane was treated with diazomethane until a constant methoxyl content was obtained. A vigorous nitrogen evolution took place and the solution became much lighter in color. The product was isolated and purified in the usual way.

Methylation of Acetic Acid Spruce Lignin with Methanol in the Presence of Hydrochloric Acid.—When 2 g. of purified acetic acid lignin was added to 50 cc. of anhydrous methanol containing 0.5% anhydrous hydrogen chloride, a portion of the lignin went into solution but, even on addition of 10 cc. of anhydrous dioxane, complete solution of the lignin did not occur. After refluxing for three hours, another 10 cc. of methanol containing 1% hydrogen chloride was added and refluxing was continued for another hour. The filtered solution was dropped into a large volume of distilled water, thus precipitating the methanol lignin. It was thoroughly washed with distilled water, dried, dissolved in dioxane, and precipitated by dropping the filtered solution into ether. The methoxyl content of the dried product after being washed with ether and petroleum ether was 19.6%.

Complete Methylation of Acetic Acid Spruce Lignin Premethylated with Diazomethane.—The methylation was carried out by the simultaneous addition of 50 cc. of dimethyl sulfate and 105 cc. of 30% sodium hydroxide to a vigorously stirred solution of 3 g. of diazomethane-methylated acetic acid lignin in 50 cc. of acetone. A constant methoxyl content (see Table II) was reached after four methylations. The product, a light yellowish brown powder, was purified in the usual way from dioxane and ether.

Saponification of Acetic Acid Spruce Lignin.—Acetic acid lignin (15 g.) was placed in an Erlenmeyer flask, the air was replaced by nitrogen, and 200 cc. of *N* sodium hydroxide solution was added. The lignin quickly went into solution and was kept at room temperature for five hours. The solution was then acidified with a small excess of hydrochloric acid, causing the lignin to precipitate. It was centrifuged and washed thoroughly with distilled water until the product was free of hydrochloric acid. The lignin was dried, dissolved in dioxane, the solution was centrifuged and filtered, and the lignin was isolated by dropping the solution into anhydrous ether. The lignin separated as a light brown powder in a yield of 14.5 g.

The toluenesulfonation and the methylation of the saponified acetic acid lignin were carried out by the methods described for the original acetic acid lignin.

Treatment of the Three Acetic Acid Lignin Fractions with 72% Sulfuric Acid.—The purified lignin fractions were subjected to a lignin determination procedure. The sample (about 1 g.) was placed in a small porcelain mortar and thoroughly mixed with 15 cc. of cold 72% sulfuric acid. The mixture was allowed to stand for two hours at 20°. The contents of the mortar were then washed into a 2-liter flask, the solution diluted to 575 cc., and refluxed for four hours. After cooling, the lignin was filtered on a tared Berlin filter crucible, dried, and weighed. The results are given in Table III.

TABLE III

LIGNIN DETERMINATIONS ON THE ACETIC ACID LIGNINS

Fraction	I	II	III	Acetic acid Willstätter lignin
Klason lignin, %	84.33	88.6	90.02	87.14
MeO of the lignin, %	14.7	14.6	13.5	16.0

Preparation of Acetic Acid Willstätter Spruce Lignin.—Willstätter spruce lignin (MeO content 15.5%), which had been kept under water in the presence of a small amount of toluene, was filtered and pressed as dry as possible. This lignin (128 g. containing 29.8 g. oven-dry lignin) was refluxed for ten hours with 1900 cc. of glacial acetic acid and 28 g. of magnesium chloride (hexahydrate). The dark brown solution was centrifuged and the small amount of residue was refluxed for four hours with 750 cc. of a fresh mixture of acetic acid and magnesium chloride. The combined acetic acid solutions were filtered through a glass fritted filter and concentrated under reduced pressure to a sirup. This was diluted with 200 cc. of a mixture of acetone and dioxane. The filtered solution was slowly dropped into four liters of distilled water with continuous stirring. The acetic acid Willstätter lignin separated as a light brown flocky precipitate, which was filtered, washed thoroughly with distillled water, and dried in a desiccator over sulfuric acid and sodium hydroxide. The yield was 27.9 g. or 96%. This crude product had a methoxyl content of 14.6%. It was purified twice in the usual way. The analyses of the acetic acid Willstätter lignin and its derivatives are given in Table I.

The dioxane–acetone–water mother liquor (light straw yellow in color) was concentrated under reduced pressure and yielded a small amount of a reddish-brown resin which was largely soluble in ether. Evaporation of the clear ether extract left a reddish sirup which reduced Fehling solution slowly in the cold and rapidly on warming. It partially crystallized and will be investigated further.

The small amount of lignin (1.2 g.) which did not dissolve in the acetic acid–magnesium chloride mixture was extracted in a Soxhlet apparatus with methanol, ether, and petroleum ether. It was light brown in color and contained 10.8% methoxyl. Upon treatment with 72% sulfuric acid, 98.6% was recovered containing 11.25% methoxyl.

The acetyl derivative (21.3% AcO) and the toluenesulfonyl ester of acetic acid Willstätter lignin were prepared as described for acetic acid spruce lignin.

Methylation of acetic acid Willstätter lignin with diazomethane was carried out as described for acetic acid spruce lignin until a constant methoxyl content was reached. This product was also toluenesulfonated.

Methylation of Acetic Acid Willstätter Lignin with Methanol and Hydrochloric Acid.—When 2 g. of acetic acid Willstätter lignin was refluxed for three hours with 100 cc. of anhydrous methanol containing 0.5% of hydrogen chloride, a portion of the lignin went into solution and the remainder resinified to a rubbery mass. The filtered solution was evaporated to dryness under reduced pressure to remove the hydrogen chloride and the residue was redissolved in methanol. On pouring this solution into distilled water, the methanol lignin derivative separated, partly forming a colloidal solution. The addition of a few grams of anhydrous sodium sulfate coagulated the lignin, which was then filtered, washed with distilled water, and dried. It was purified in the usual way, giving a violet-brown powder.

Complete Methylation of Diazomethane-Methylated Acetic Acid Willstätter Lignin.—This methylation was carried out by the method used for acetic acid spruce lignin until a constant methoxyl content was obtained. After purification in the usual manner, the fully methylated derivative was a light orange-yellow powder.

Saponification of Acetic Acid Willstätter Spruce Lignin.—Crude acetic acid Willstätter spruce lignin (10 g.) was dissolved in 30 cc. of dioxane and the air in the flask was replaced by nitrogen. A solution of 5 g. of sodium hydroxide in 100 cc. of water was then added. The clear dark reddish-brown solution was kept at room temperature for four hours, the solution was diluted with 150 cc. of water, and a solution of 15 cc. of concentrated hydrochloric acid in 100 cc. of water was added, causing the precipitation of the lignin. The latter was centrifuged, washed in the centrifuge jar, filtered on a Büchner funnel, and washed thoroughly. The product was partially dried in a desiccator over sodium hydroxide and the still moist lignin was dissolved in dioxane. The water in the solution was removed by distilling off a part of the solution *in vacuo* with intermediate addition of fresh dioxane. The solution was then made up with dioxane to 120 cc., centrifuged, and filtered. The lignin was precipitated from this solution by dropping it into anhydrous ether. The product was purified in the usual way.

The toluenesulfonyl derivative, the diazomethane-methylated product, and the toluenesulfonyl derivative of the latter were prepared as the corresponding derivatives of the unsaponified acetic acid Willstätter lignin; their analyses are given in Table II.

The authors are indebted to Mr. Sewell T. Moore, who carried out preliminary experiments on acetic acid Willstätter lignin and to William C. Martin, who carried out the treatments of the acetic acid lignins with 72% sulfuric acid and a part of the analyses.

Summary

Acetic acid spruce lignin and acetic acid Willstätter spruce lignin have been compared with isolated native spruce lignin. It is found that the number of hydroxyl groups in the acetic acid lignins is the same as that in the isolated native spruce lignin, indicating that no new hydroxyl groups are formed when lignin is extracted from spruce by means of acetic acid.

APPLETON, WISCONSIN RECEIVED OCTOBER 9, 1944