filtrate was evaporated to a sirup and the latter dissolved in 75 cc. of hot ethyl acetate and filtered hot. The clear solution, after two days at 0°, deposited a small quantity of crystalline material. This was recrystallized from 50 cc. of ethyl acetate, and finally from a few cc. of ethyl alcohol. The final product possessed the correct m. p. (140–141°) and specific rotation (186° in water solution) of α-ethylgalactopyranoside.

(b) Four grams of ethylglucofuranoside sirup ($-54°$) was dissolved in 100 cc. of ethyl alcoholic hydrogen chloride. After one hour's refluxing, the observed rotation shifted from an initial value of -4.55 to $+8.65°$ in a 2-dm. tube. After one more hour of refluxing, the solution was neutralized with silver carbonate and filtered. The filtrate was evaporated to a sirup, which was dissolved in 10 cc. of ethyl alcohol. After two days at $-10°$, the solution crystallized to a solid mass. The crystals were filtered and recrystallized from 25 cc. of acetone. After being dried at 15 mm. and 58°, the crystals melted at 70–72° and had a specific rotation of 138° in water. Further recrystallizations did not change this value, which agreed closely with that given by Fischer[20] in his first preparation of α-ethylglucopyranoside.

Summary

A new synthesis for alkylfuranosides has been found. From galactose ethylmercaptal, β-ethylgalactofuranoside can be prepared in 70% yield by treatment with mercuric chloride and mercuric oxide at 20° in absolute ethyl alcohol. The benzylmercaptal will give a similar yield.

The same reaction with glucose mercaptals apparently goes in two stages. The first, to an α-alkylthioglucofuranoside, goes very fast, even at 0°. The second stage, to the glucofuranoside, is slow at 20°, but goes fairly fast at 70°. A sirupy mixture of α- and β-ethylglucofuranoside results.

The α-ethyl- and α-benzylthioglucosides isolated in the first stage of the reaction are furanosides, and not of normal structure as earlier workers believed. This is shown by acid hydrolysis constants, conversion into ethylglucofuranoside, and calculations from Hudson's rules of isorotation.

The effect of acidity on these reactions has been shown by the conversion of furanosides into pyranosides in alcoholic hydrogen chloride.

PRINCETON, NEW JERSEY RECEIVED APRIL 28, 1937

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[20] Fischer, *Ber.* **27**, 2480 (1894).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF HAWAII]

The Properties of Bagasse Lignin Extracted by the Dilute Nitric Acid Method

BY JOHN H. PAYNE, EDWARD FUKUNAGA AND RUTH KOJIMA[1]

The ease with which lignin can be extracted from bagasse by the use of dilute nitric acid[2] renders the method of definite value in studying the composition of lignin from this source. Since any extraction method probably brings about some change in the lignin,[3] the change produced by dilute nitric acid, which involves mild nitration, is undoubtedly not greater than that produced by more drastic reagents.[4] Furthermore the introduction of a small amount of nitrogen in the form of nitro groups renders the lignin molecule more soluble in many organic solvents, and furnishes a method of estimating the empirical molecular weight.

It was found[2] that bagasse, which had been freed from gums, waxes, and water-soluble compounds, undergoes practically no change when heated to a temperature of 98–100° for several hours with 1.25% nitric acid. If the concentration of nitric acid is increased to 1.50%, however, definite reaction occurs. After one hour the bagasse is uniformly orange in color, and subsequent boiling with 1% sodium hydroxide dissolves the lignin, leaving the cellulose free. Upon acidification of the sodium hydroxide solution, the lignin is precipitated as a dark brown sticky mass. With concentrations of nitric acid above 1.50% the results are similar except that there is evidence of greater nitration, and greater decomposition of cellulose occurs; 1.40% nitric acid was found to be the minimum concentration which would effect uniform nitration of the bagasse, and which would cause the lignin to go into solution in 1% sodium hydroxide solution.

These results seem to indicate that a definite minimum concentration of nitric acid is necessary to bring about nitration of the lignin. The lignin thus nitrated is soluble in dilute sodium hydroxide solution. The orange color of the nitrated bagasse is due only in part to the color of the nitro-

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[1] University of Hawaii Graduate Scholar.

[2] Payne, *Ind. Eng. Chem.*, **26**, 1339 (1934).

[3] Wright and Hibbert, THIS JOURNAL, **59**, 125 (1937).

[4] Hilpert and co-workers, *Ber.*, **67**, 1551 (1934); **68**, 16, 371, 380 (1935).

lignin, however, since picric acid can be recovered by extracting the dried nitrated bagasse with benzene. The isolation of picric acid demonstrates the presence of aromatic compounds in the cellulose–lignin complex.

The crude nitrated lignin is obtained in yields which average 12% on the basis of the dry bagasse. The lignin content of the bagasse, as determined by the customary sulfuric acid method at 0°, is approximately 20%. This difference is probably due to the solubility of some of the products of the lignin nitration in the acidic solution. The precipitated product is soluble in ethanol, 1,4-dioxane, and the ethers of ethylene glycol. The solubility is greatly increased by the presence of a small amount of water, the completely dried material being difficultly soluble.

Purification of the vacuum dried lignin is readily accomplished by repeated precipitation from solution in anhydrous 1,4-dioxane by addition of anhydrous ether. The lignin reaches a constant composition after five precipitations. Analysis of the crude and purified lignin is given in Table I. Table II shows the quantities lost in each step of the purification.

TABLE I

ANALYSIS OF LIGNIN

	C, %	H, %	N, %	OH, %	OCH_3, %
Pptd. once from ethanol			2.93	4.19	17.5
Pptd. five times from dioxane			1.77	4.20	14.7
Pptd. six times from dioxane	55.77	5.27	1.77	4.19	14.7
Methoxylated					27.3

TABLE II

FRACTIONATION OF CRUDE LIGNIN BY USE OF DIOXANE–ETHER

Fractionation	Amount used, g.	Ether–dioxane insoluble, g.
1	15.0	6.5
2	6.5	6.0
3	6.0	5.6
4	5.6	5.5
5	5.5	5.4

The purified lignin is a very light, electrostatic, tan-colored product. It is soluble in 1,4-dioxane, and the ethers of ethylene glycol, but insoluble in other organic solvents. The nitrogen content of 1.77% corresponds to an empirical molecular weight of 791. This minimum unit contains approximately two hydroxyl groups and four methoxyl groups.

Since the purified lignin was readily soluble in anhydrous 1,4-dioxane, molecular weight determinations by the freezing point method were made. The results of these are given in Table III.

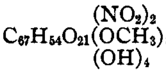
TABLE III

MOLECULAR WEIGHT OF LIGNIN

Trial	Weight of lignin, g.	Weight of dioxane, g.	F.-p. depression, °C.	Mol. wt.
1	0.2696	21.92	0.033	1750
2	.4743	13.78	.100	1620
3	.3111	21.33	.050	1490
4	.4467	26.04	.053	1520
5	.4743	17.66	.044	1860
			Average	1650

The average molecular weight is shown to be 1650 or approximately twice the empirical molecular weight calculated from the nitrogen content. This value is roughly one-half of the 3900 ± 300 value recently determined by Loughborough and Stamm,[5] using boiling-point and osmotic pressure methods with wood lignins extracted by three different methods. Attempts to determine the equivalent weight of the substance by electrometric titrations gave titration curves with no sharp breaks, indicating the absence of strongly acidic groups such as the carboxyl.

On the basis of these data and assuming the nitrogen to be present entirely in the form of nitro groups, the dilute nitric acid lignin has a molecular weight of approximately 1600 and the following approximate composition



$$C_{67}H_{54}O_{21}\begin{matrix}(NO_2)_2\\(OCH_3)_8\\(OH)_4\end{matrix}$$

This formula indicates a considerably smaller number of hydroxyl groups than are found in other lignins.[6] Some doubt exists as to whether the pyridine method used results in complete acetylation of all hydroxyl groups. Since, however, drastic acetylation methods were found apparently to bring about the formation of hydroxyl groups of lignin, the pyridine method is probably as reliable a method as is available.

Alkaline methoxylation has been found by Hibbert and co-workers[3,7] likewise to be unreliable as a measure of original hydroxyl content, since hydroxyl groups appear to be formed by the alkali. This fact was confirmed by methoxylation of the purified nitric acid lignin. The methoxylation gave a product containing 27.3% methoxyl,

(5) Loughborough and Stamm, *J. Phys. Chem.*, **40**, 1113 (1936).

(6) Brauns and Hibbert, THIS JOURNAL, **55**, 4720 (1933).

(7) Compton and Hibbert, *Can. J. Research*, **B15**, 38 (1937).

as shown in Table I, a value which would indicate the presence of approximately four hydroxyl groups in the original empirical formula, rather than the two shown by acetylation. Obviously definite changes occur in the lignin structure during both acetylation and methoxylation.

Attempts to determine the relationship of the nitrogen to the other groups are under way.

Experimental

Preparation of Dilute Nitric Acid Lignin.—One hundred-gram samples of previously extracted (2:1 benzene–ethanol mixture, followed by water) Hawaiian bagasse were heated for one hour in covered Pyrex beakers with 1000 cc. of 1.42% nitric acid at a temperature of 98–100° maintained by a boiling water-bath. The orange colored bagasse was filtered from the acid solution, washed thoroughly with water and air dried. (In spite of repeated washing, the wash water was invariably yellow.) The dried bagasse was extracted again with a 2:1 benzene–ethanol solution in order to remove picric acid.

The nitrated bagasse after extraction was suspended in 1% sodium hydroxide solution and heated just to boiling. The dark brown solution was filtered from the cellulose residue and the latter washed several times with hot water. The combined filtrates were then acidified with dilute hydrochloric acid and the dark brown lignin thus precipitated allowed to settle. The supernatant liquid was poured off, the precipitate filtered and washed thoroughly with hot water. The crude product was finally dried *in vacuo* at 60°. An average yield of 12 g. was obtained.

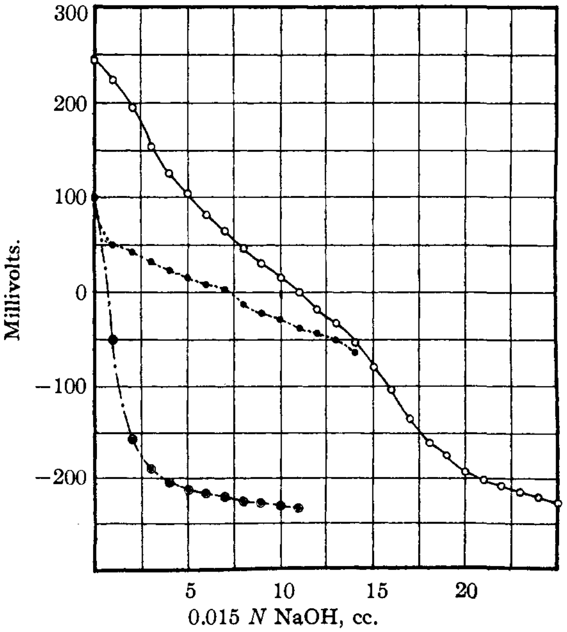


Fig. 1.—Electrometric titration curves: nitrolignin -○—○-, *o*-nitrophenol ---●----●---, blank -◉---◉---.

Purification of Lignin.—To 250 cc. of pure anhydrous 1,4-dioxane was added with shaking 10 g. of the crude lignin. After standing for several hours with occasional shaking, the solution was centrifuged and filtered. An insoluble dark brown gelatinous residue remained on the filter. The reddish-brown filtrate was added dropwise with vigorous stirring to ten times its volume of anhydrous diethyl ether. The tan-colored lignin thus precipitated was separated by centrifuging and filtration. After washing several times with dry ether, the lignin was finally washed with petroleum ether, and dried *in vacuo* at 60°. This procedure was repeated five times.

Analysis of Lignin.—Ultimate micro analyses were made by Dr. Ing. A. Schoeller. Methoxyl determination was macro by the usual Zeisel procedure. Macro hydroxyl group determinations were made both by the pyridine–acetic anhydride method, and by the method of Liebermann and Hörmann.[8] The latter method, which involves heating the sample with acetic anhydride and sodium acetate to 100°, gave abnormally high results. The product thus acetylated was insoluble in cold alcoholic potassium hydroxide even after several days' standing. It dissolved only slowly in the boiling solution. Calculation of hydroxyl content by this method based upon cold hydrolysis gave an average of 9.0%, while based upon hot hydrolysis 16.9%—values which are roughly twice and four times, respectively, the percentage obtained by the pyridine method. It is probable that this drastic acetylation method brings about the introduction of a greater quantity of acetyl groups than corresponds to the number of hydroxyl groups originally present. The accepted data given in Table I, therefore, are by the pyridine method.

Molecular Weight Determination.—Anhydrous 1,4-dioxane was prepared by the method of Kraus and Vingee.[9] The customary Beckmann freezing-point apparatus was modified for use of small quantities of solution, and was arranged so that a current of dry nitrogen could be passed through the apparatus in order to prevent the absorption of moisture from the atmosphere by the dioxane. The sample of lignin and the dioxane were weighed directly into the freezing tube. Even with these precautions some absorption of moisture occurred occasionally after continued standing. This was evidenced by a rise in the maximum points of the cooling curves. Such determinations were discarded. The results are given in Table III. The constant 4.70 was used in the calculations. The average deviation of the results is 125.

Electrometric Titration.—One-tenth gram samples of the purified lignin were dissolved in 170 cc. of a 1 to 1 dioxane–water mixture. The solution was titrated electrometrically using a glass electrode with 0.015 *N* sodium hydroxide solution. The average of a series of titration curves is shown in Fig. 1 along with a similar curve for *o*-nitrophenol and the blank dioxane–water curve. It will be noted that no break occurs in the curve, although there is some change in slope. Carboxyl groups are not indicated.

Methoxylation of Lignin.[10]—The purified lignin was methoxylated by the method of Compton and Hibbert[7] using dimethyl sulfate with a slight excess of alkali at a

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[8] Mayer, "Analyse und Konstitutionsermittlung organischer Verbindungen," 5th ed., Verlag von Julius Springer, Berlin, 1930, p. 333.

[9] Kraus and Vingee, THIS JOURNAL, **56**, 511 (1934).

[10] The experimental work of this section was performed by Mr. David Takahashi.

temperature of 20°. The methoxylated product, purified by precipitation from anhydrous 1,4-dioxane with anhydrous ether, was obtained as a light buff colored powder. Analysis by the Zeisel method of five different samples gave an average of 27.3% methoxyl as shown in Table I.

Summary

1. A method for extracting the lignin in bagasse by means of dilute nitric acid is described.

2. The lignin extracted by this method has an apparent molecular weight by the freezing-point method in 1,4-dioxane of 1650 ± 125 and has the following approximate formula: $C_{87}H_{54}O_{21}(NO_2)_2(OCH_3)_8(OH)_4$.

3. Methoxylation and acetylation data confirm the unreliability of these methods in determining the percentage of hydroxyl in the lignin molecule.

4. The absence of carboxyl groups is indicated from electrometric titration curves.

HONOLULU, HAWAII RECEIVED APRIL 6, 1937

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Heat Capacity and Entropy of Silver Nitrate from 15 to 300°K. The Heat and Free Energy of Solution in Water and Dilute Aqueous Ammonia. The Entropy of Silver Ammonia Complex Ion

BY WENDELL V. SMITH, OLIVER L. I. BROWN AND KENNETH S. PITZER

The data necessary to compute an accurate value for the free energy of solution and free energy of formation of crystalline silver nitrate are complete except for a calorimetric determination of the heat of solution and entropy of the salt. In view of this we have determined the heat capacity of the solid over the temperature interval from 15 to 300°K. and from this have calculated its entropy. We have determined its heat of solution in water and, by combining these and previously available data, have calculated its free energy of solution and the free energy of formation of solid silver nitrate from its elements. We have also determined the heat of solution of silver nitrate in dilute aqueous ammonia and, by combining this with other data already available, have obtained a value for the entropy of aqueous silver ammonia complex ion.

Material.—A "chemically pure" grade of silver nitrate was recrystallized from distilled water and dried in an oven at 130°C. for thirty-six hours. The heat capacity measurements through the ice-point showed that it contained not more than 0.02% water.

Heat Capacity Measurements.—The heat capacity measurements were made with a calorimeter and cryostat similar to that described by Latimer and Greensfelder.[1] In calculating the heat capacities and in the subsequent heat of solution calculations one calorie was taken equal to 4.1833 int. joules, and the molecular weight of silver nitrate was taken as 169.89. Measurements were made on a sample of 193.57 g. (weight *in vacuo*) of the silver nitrate. The results are given in Table I and shown as a function of temperature in Fig. 1.

TABLE I

MOLAL HEAT CAPACITY OF SILVER NITRATE

T, °K.	C_p Cal./deg./mole	T, °K.	C_p Cal./deg./mole
13.25	1.14	140.02	16.56
15.16	1.60	145.32	16.81
18.01	2.20	150.93	17.03
21.38	2.86	156.78	17.24
24.27	3.40	164.02	17.54
27.32	4.10	169.40	17.70
30.61	4.84	175.05	17.90
34.62	5.56	180.71	18.18
38.78	6.43	186.66	18.41
52.87	9.00	192.59	18.62
58.18	9.76	198.74	18.87
63.29	10.61	205.03	19.12
68.51	11.31	211.54	19.38
74.01	11.95	218.31	19.61
80.09	12.62	225.37	19.83
86.23	13.19	232.31	20.11
92.01	13.68	239.15	20.30
97.76	14.15	246.22	20.55
108.12	14.91	253.77	20.79
113.35	15.27	261.50	21.06
118.78	15.57	268.76	21.35
124.16	15.81	275.78	21.65
129.18	16.03	283.46	21.82
134.34	16.32	291.36	22.05
		296.62	22.19

Entropy of Silver Nitrate.—The entropy was calculated by the graphical integration of a plot of C_p *vs.* log T, combined with an extra-

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(1) Latimer and Greensfelder, THIS JOURNAL, 50, 2202 (1928).